



Mechanism investigation and stable isotope change during photochemical degradation of tetrabromobisphenol A (TBBPA) in water under LED white light irradiation

Jukun Xiong^{a, b}, Guiying Li^a, Ping'an Peng^b, Faina Gelman^c, Zeev Ronen^d, Taicheng An^{a, *}

^a Guangdong Key Laboratory of Environmental Catalysis and Health Risk Control, Guangzhou Key Laboratory of Environmental Catalysis and Pollution Control, School of Environmental Science and Engineering, Institute of Environmental Health and Pollution Control, Guangdong University of Technology, Guangzhou, 510006, China

^b State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, China

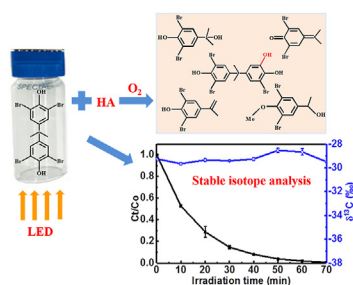
^c Geological Survey of Israel, 30 Malhei Israel Street, Jerusalem, 95501, Israel

^d Zuckerberg Institute for Water Research, Department of Environmental Hydrology and Microbiology, The Jacob Blaustein Institutes for Desert Research, Ben-Gurion University of the Negev, Sede Boqer Campus, Sede Boqer, 84990, Israel

HIGHLIGHTS

- A LED white light was employed to model the photochemical degradation of TBBPA.
- Humic acid was excited to promote the elimination of TBBPA in water.
- ¹O₂ yield from humic acid excited was the dominated reactive species in this system.
- Four dibrominated intermediates and hydroxyl-tribromobisphenol A were identified.
- No significant C isotope fractionation was obtained during photochemical degradation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 29 February 2020

Received in revised form

7 June 2020

Accepted 8 June 2020

Available online 13 June 2020

Handling Editor: Klaus Kümmerer

Keywords:

Tetrabromobisphenol A

Humic acid

Photochemical degradation

Degradation mechanism

ABSTRACT

Light driven degradation is very promising for pollutants remediation. In the present work, photochemical reaction of tetrabromobisphenol A (TBBPA) under LED white light ($\lambda > 400$ nm) irradiation system was investigated to figure out the TBBPA photochemical degradation pathways and isotope fractionation patterns associated with transformation mechanisms. Results indicated that photochemical degradation of TBBPA would happen only with addition to humic acid in air bubbling but not in N₂ bubbling. For photochemical reaction of TBBPA, singlet oxygen (¹O₂) was found to be important reactive oxygen species for the photochemical degradation of TBBPA. 2,6-Dibromo-4-(propan-2-ylidene)cyclohexa-2,5-dienone and two isopropyl phenol derivatives were identified as the photochemical degradation intermediates by ¹O₂. 2,6-Dibromo-4-(1-methoxy-ethyl)-phenol was determined as an intermediate via oxidative skeletal rearrangement, reduction and O-methylation. Hydrolysis product hydroxyl-tribromobisphenol A was also observed in the reductive debromination process. In addition, to deeply explore the mechanism, carbon and bromine isotope analysis were performed using gas chromatography/combustion/isotope ratio mass spectrometry (GC/C/IRMS) and gas chromatography-multicollector inductively coupled plasma mass spectrometry (GC/MC/ICPMS) during the photochemical degradation of

* Corresponding author.

E-mail address: antc99@gdut.edu.cn (T. An).

Carbon stable isotope
Bromine stable isotope

TBBPA. The results showed that photochemical degradation could not result in statistically significant isotope fractionation, indicated that the bond cleavage of C-C and C-Br were not the rate controlling process. Stable isotope of carbon being not fractionated will be useful for distinguishing the pathways of TBBPA and tracing TBBPA fate in water systems. This work sheds light on photochemical degradation mechanisms of brominated organic contaminants.

© 2020 Elsevier Ltd. All rights reserved.

1. Introduction

As an extensive use of reactive flame retardants in a variety of products such as insulated wires, printed circuit boards, and polycarbonated plastics, tetrabromobisphenol A (TBBPA) is among a highest yield and current-use brominated flame retardants (BFRs) (Li et al., 2016b; Fan et al., 2017). TBBPA's wide utilization has resulted in its ubiquitous presence in the aquatic environments (Huang et al., 2016). Owing to its lipophilicity and bioaccumulation (Reistad et al., 2005), TBBPA could be carried in organisms and human tissues (Morris et al., 2004; Nakao et al., 2015). Unfortunately, TBBPA is also considered to be one of the endocrine-disrupting chemicals with multiple hormonal activities (de Wit et al., 2010).

Because of wide utilization as well as possible risks of TBBPA, there is a pressing need to effectively attenuate TBBPA and other BFRs from the contaminated environments. In the past few years, many methods have been demonstrated to eliminate them effectively, including photochemical (Wang et al., 2015), biodegradation (Li et al., 2016a; Chen et al., 2020b) and advanced oxidation technology (Zhou et al., 2020). Photochemical degradation processes have demonstrated its great ability to efficiently degrade the persistence organic contaminants in the aquatic environments (Amina et al., 2020; Chen et al., 2020a; Garcia-Muñoz et al., 2020; Zhang et al., 2020). Upon exposure to sunlight, organic pollutants could be degraded via the generation of chemical transients (singlet oxygen, hydroxyl radicals, solvated electrons, oxyl and peroxy radicals and excited triplet states) (Aguer et al., 2005). The white light ($\lambda > 400$ nm) irradiation was part wavelength of sunlight which is very abundant and renewable light energy. Nevertheless, the elimination of TBBPA, the recognition as well as elucidation of complicated photochemical reaction pathways of TBBPA with white light irradiation, and the final environmental fate of TBBPA in aquatic environments still face many challenges.

By measuring shift in the isotope composition, compound specific isotope analysis (CSIA) could be employed to probe transformation as well as the fate of various organic pollutants in the environments (Meckenstock et al., 2004; Elsner, 2010). For instance, CSIA was employed with success to distinguish the transformation mechanism of organic compounds, including polycyclic aromatic hydrocarbons (Kuemmel et al., 2016) and chlorobenzenes (Passeport et al., 2018). In general, an enrichment of heavy isotope (e.g., ^{13}C) is observed in the remaining substrate when transformation of organic pollutants was taken place. Using an experimental determination of isotopic fractionation, the change of the isotope ratio during the organic pollutants transformation process could quantitatively evaluate the changes in environments (Maier et al., 2016; Torrentó et al., 2017). Usually, single-element isotopic fractionation was used to be an indicator for a certain transform route no requirement for tracing intermediates, which is a challenge in the sophisticated systems, for instance in the real environment. Nevertheless, potentially multi-element isotopic fractionation enables the isotope ratios of multiple elements to be correlated, and discloses the information of

specific pathways (Kuntze et al., 2016). Recent researches showed that multi-element CSIA, along with analyzing two isotope ratios ($\text{D}/^1\text{H}$ and $^{13}\text{C}/^{12}\text{C}$ or $^{37}\text{Cl}/^{35}\text{Cl}$) could be a particularly valuable tool to identify photochemical transformation mechanisms and probe the fate of many organic contaminants, including ethylene dibromide (Kuntze et al., 2016), benzene toluene ethylbenzene and xylene (Fischer et al., 2008), and chlorinated ethenes (Wiegert et al., 2013). However, isotopic fractionation of typical BFRs (such as TBBPA) under white light irradiation in aquatic environment has not been attempted yet. Nevertheless, the dual elements analysis of carbon and bromine isotope (e.g., $^{13}\text{C}/^{12}\text{C}$ and $^{81}\text{Br}/^{79}\text{Br}$) of TBBPA is recognized as a working tool to differentiate mechanism of its transformation as well as to monitor its source and fate in field or in lab.

The present work was aimed to investigate whether photochemical degradation of TBBPA under white light ($\lambda > 400$ nm) irradiation system happened. LED lamps were used to simulate white light. Furthermore, photochemical kinetics of TBBPA were also evaluated with different initial pH values, and the possible degradation mechanism of TBBPA with humic acid system were proposed based on reactive oxygen species (ROSs) scavenging and the identified degradation intermediates. The occurrence of carbon and bromine isotopic fractionation was also investigated to differentiate degradation mechanism and detect the transformation during the photochemical degradation processes. This work is also expected to provide useful information for the degradation of TBBPA and other brominated organic contaminants in LED white light irradiation system.

2. Materials and methods

2.1. Materials

TBBPA (purity $> 99\%$) was obtained from sigma-aldrich (St. Louis, MO, USA). Silylating reagent *N,O*-bis(trimethylsilyl)trifluoroacetamide/trimethylchlorosilane (BSTFA:TMCS, 99:1, v/v, supelco-33148) was purchased from accustandard Inc. (New Haven, CT). Humic acid was purchased from J&K scientific Ltd, China, and employed to study the influence of natural organic material on photochemical degradation of TBBPA. Sodium azide (NaN_3), furfuryl alcohol (FA) and all other chemicals were at least reagent grade, which were purchased from Guangzhou chemical reagent Co., Inc., China. HPLC grade of methanol (MeOH), hexane, as well as dichloromethane were purchased from CNW technologies (ANPEL scientific instrument Co., Ltd, China). Acetone (HPLC grade) was obtained from J. T. Baker (Center Valley, PA, USA). Catalase (CAT) and superoxide dismutase (SOD) were purchased from sangon biotech (Shanghai) Co., Ltd. Polycarbonate filters were from Millipore (0.22 μm , 47 mm).

2.2. Photochemical degradation experiments

The photochemical degradation experiments were conducted under LED white light irradiation (PCX50A Discover, Perfectlight

Scientific Pty Ltd, Beijing, China) and were performed in triplicate. The power was set as 5 W and the wavelength of white light was > 400 nm. The switching time was set as 0.01 s. The quartz tube reactor was used throughout in these experiments, and nine channels were performed at the same time. TBBPA (5 mg L⁻¹, 50 mL) was employed to assess the photochemical degradation efficiencies. The preparation of humic acid was carried out with addition of 0.1 g humic acid into 500 mL solution, and then filtered by using polycarbonate filter. Then the reaction system was irradiated by LED white light with the temperature maintaining at (25 ± 1) °C. The photochemical degradation of TBBPA with different initial pH were also studied, and the adjustment of pH values was carried out with addition of NaOH (1 M) or HCl (1 M).

2.3. Measurement of ROSs

Recording the electron parameter resonance (EPR) spectra with the wavelength ranging from 200 to 2000 nm were performed using a Bruker EMX Plus-10/12 (Switzerland). EPR measurements were carried out with G modulation amplitude, at 10 mW and with modulation frequency of 100 kHz. Sample (100 µL) was put in quartz flat cells and then placed inside the microwave cavity of spectrometer, which was illuminated directly with a 20 mW mercury lamp. The irradiation from mercury lamp was passed through a path-length liquid filter (30 mm, λ > 400 nm; solution containing Na₂CO₃ (1 g L⁻¹), NaNO₂ (48.4 g L⁻¹), K₂CrO₄ (0.2 g L⁻¹)). The hyperfine coupling constant could be achieved from the spectra by accumulation, simulation as well as optimization using software (Han et al., 2016). The DMPO (5,5-Dimethyl-1-pyrroline N-oxide) of 100 mmol L⁻¹ was employed to trap the O₂⁻ as well as •OH. While TEMP (2,2,6,6-tetramethyl-4-hydroxy-piperidinyl-oxyl, 10 mmol L⁻¹) was used to trap ¹O₂ (Bao and Niu, 2015). Double-deionized water was used to trap •OH and ¹O₂, while MeOH of HPLC grade was used to trap O₂⁻ radicals. The period between reaction initiation and start of EPR scanning was maintained ≤ 2 min.

2.4. Analytical determination

HPLC analysis: The concentration of TBBPA during the photochemical degradation were measured using HPLC (Agilent 1260) and SinoPak C18 column (4.6 mm i.d. × 150 mm, 5 µm) was used as the column. Detailed detection conditions were similar to our previous works (An et al., 2011; Zu et al., 2014). The wavelength of UV detector was set at 210 nm, and 20 µL of the sample was injected into the column. The temperature of the column was programmed at 30 °C. Mobile phase was selected as 80% MeOH and 20% acidified water (2% glacial CH₃COOH, v/v) and the flow rate was set to 0.8 mL min⁻¹.

GC/MS analysis: The photochemical intermediates of TBBPA were identified using a Agilent 7890 gas chromatography using a Agilent 5975 mass selective detector (GC/MS). The column was DB-5 ms column (0.25 mm i.d. × 30 m, 0.25 µm). Detailed detection conditions were similar to our previous works (An et al., 2011; Huang et al., 2016). For direct detection of intermediates, the samples were dissolved in 1.0 mL acetone and then sample (1 µL) was analyzed using GC/MS. The polar intermediates produced during the photolysis were also identified with GC/MS after the samples were derivatized. The detailed information about this is provided in the supporting information.

HPLC/TOF/MS analysis: The photochemical degradation intermediates of TBBPA were also identified using a HPLC with a triple-stage quadruple time-of-flight MS (HPLC/TOF/MS, Thermo Fisher Scientific, USA). The detailed analysis information is provided in the supporting information.

Analysis of stable C isotope: The analysis of C isotope was carried out using a GC (Trace GC Ultra; Thermo Scientific, Germany) coupled with a delta V Plus isotope ratio MS (ThermoFinnigan, Germany) through the GC Combustion Interface III (Thermo Electron, Germany) (GC/C/IRMS). The GC system was equipped with a DB-5 ms column (0.25 mm i.d. × 30 m, 5 µm, J&W scientific, USA). Detailed detection conditions were similar to our previous work (Xiong et al., 2015). Samples were all analyzed more than three times; the standard deviation were usually < 0.5‰ (1σ). δ¹³C_{V-PDB} value of sample was evaluated according to the internal laboratory standard carbon dioxide gas.

Analysis of stable Br isotope: Br isotope was analyzed using GC with multi-collector inductively coupled plasma mass spectrometer (GC/MC/ICPMS) based on the instrumental setup described early (Bernstein et al., 2013; Kuntze et al., 2016).

Calculations: The isotopic fractionation analysis was carried out based on carbon isotope composition of TBBPA during the TBBPA photochemical degradation process. The Eq. (1) was employed to correlate between the degree of degradation and change of isotope composition (Elsner et al., 2005).

$$\ln\left(\frac{R_{x,t}}{R_{x,0}}\right) = \ln f \times \epsilon \quad (1)$$

In this equation, *f* represents the fraction of the remaining fraction of TBBPA (described as *C/C₀*, where *C₀* represents TBBPA concentration at time 0; *C* represents TBBPA concentration at time *t*); *ε* represents a compound-average (bulk) isotope enrichment factor obtained from TBBPA; *R_x* represents the C isotope composition in TBBPA at time 0 and *t*.

The enrichment factor of C isotope (*ε*) was obtained as slope of linear regression line of natural logarithm of isotope enrichment; *R_{x,t}/R_{x,0}* against the natural logarithm of the extent of photochemical degradation; *f*, regression is not forced to origin. To further learn the mechanisms of the photochemical degradation of TBBPA, *ε* is converted into apparent kinetic effect (AKIE) on the basis of Eq. (2) (Kozell et al., 2015):

$$\text{AKIE} = \frac{1}{1 + z \times \frac{n}{x} \times \epsilon} \quad (2)$$

In this equation, *z* represents the intramolecular competitive position number; *n* represents the total number of atoms in molecule; *x* represents the of reactive position number.

Data analysis: Photochemical degradation efficiency of TBBPA can be figured out as TBBPA level after degradation divided by TBBPA level before the reaction, and then 100 times over. The statistical package for social sciences v18.0 software (SPSS Inc. IL, USA) was used for statistical analyses.

3. Results and discussion

3.1. Photochemical degradation kinetics of TBBPA

Photochemical reaction was one of the most important transformation processes of organics in surface aquatic environments. Thus, the photochemical transformation of TBBPA under LED white light (λ > 400 nm) irradiation were investigated in water. The results found that TBBPA could not be directly degraded without adding humic acid under 12 h irradiation (Fig. 1a), while 100% of TBBPA has been degraded with adding humic acid under 45 min irradiation (Fig. 1b). That is, TBBPA only could be degraded indirectly with sensitizing of humic acid rather than direct degradation. As showed in Figs. S1 and S2, the absorption wavelength of TBBPA is < 350 nm and the spectral irradiance of LED white light

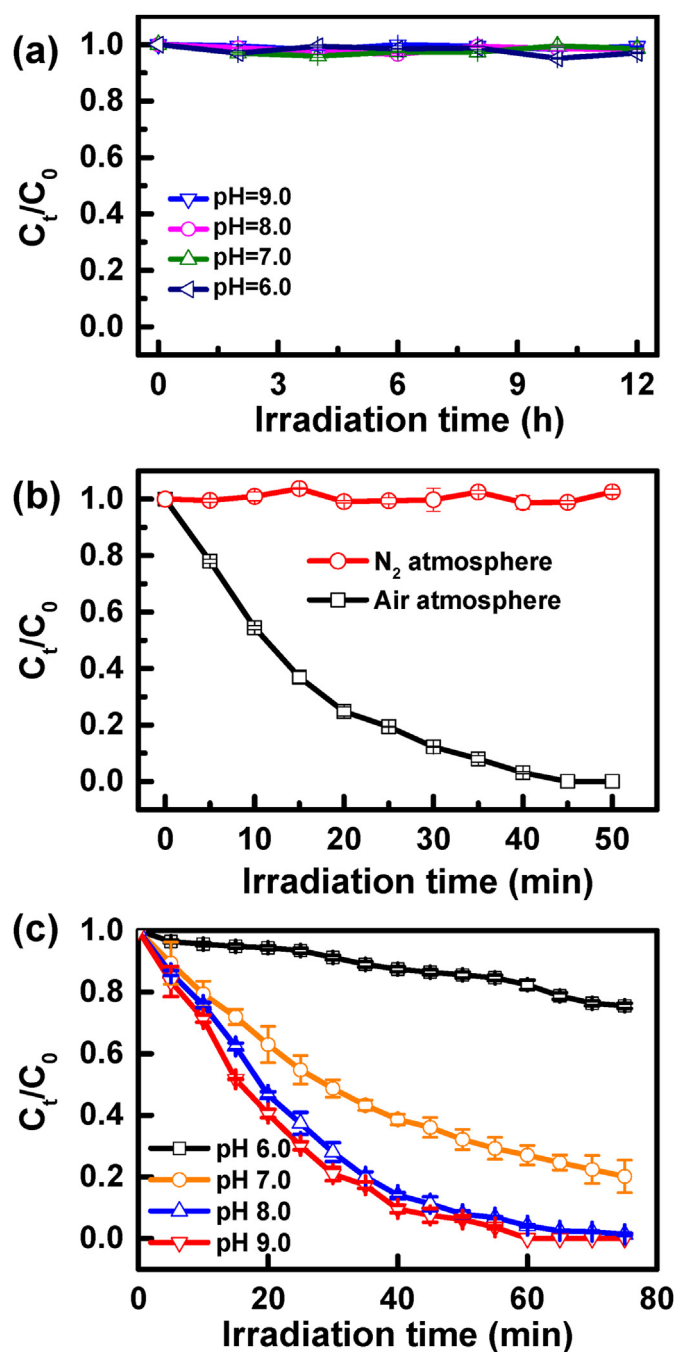


Fig. 1. The photolysis of TBBPA (error bars represent standard deviations): (a) without adding humic acid; (b) with adding humic acid; (c) effect of initial pH values on the photolysis of TBBPA.

is > 400 nm, meaning that TBBPA did not absorb the LED white light and has not been degraded directly or has been degraded very slowly in aquatic environment under LED white light. When TBBPA was irradiated with LED white light in the presence of humic acid, the photochemical degradation of TBBPA was obviously obtained in air bubbling but not in N_2 bubbling (Fig. 1b). TBBPA might be photochemically degraded indirectly due to the humic acid absorption of LED white light because TBBPA possesses two absorption peaks at 210 and 320 nm, but no absorption at wavelength > 350 nm (Fig. S1). Contrary to the results of TBBPA, the optical absorption of humic acid extended to wavelength > 400 nm, in which

LED white light has two spectral irradiances (Fig. S2). Thus, the absorption of light energy by humic acid may be the main reason why the photochemical degradation of TBBPA happened. Many published works on the photochemical reaction of organic pollutants with addition of humic acid in aquatic solution suggested that humic acid serves as a precursor or weak sensitizer to generate the reactive species, such as 1O_2 , $O_2^{\cdot-}$, and H_2O_2 in water systems (Han et al., 2009, 2016), which could trigger the photochemical degradation of pollutants.

Further, the photochemical degradation of TBBPA could be greatly influenced by the initial pH values. The degradation efficiencies increased sharply with increasing pH, while the efficiencies increased slowly above pH 8.0 (Fig. 1c). Han et al. studied the effect of pH (ranging from 6.8 to 9.0) on TBBPA photochemical degradation by illuminating TBBPA with addition humic acid in solution with different pH (Han et al., 2016), suggesting that photochemical degradation efficiencies of TBBPA were improved with the increase of the light intensity and pH values because of the hydrophobic property of the TBBPA with $pK_{a1} = 7.5$ and $pK_{a2} = 8.5$ (Howe and Dobson, 2005). When the pK_a of the TBBPA is above the pH values of the solution, the quantum yield of TBBPA photochemical decomposition decreased as the decrease of the pH; whereas as the pK_a of the TBBPA is below the pH values of the solution, photochemical decomposition is not related to the pH value. The results of our study of different pH values were similar with the previous results (Han et al., 2016).

3.2. Photochemical degradation mechanism

At pH 9.0, TBBPA has two maximum absorption peaks at 210 and 320 nm, but without absorption > 350 nm was observed (Fig. S1). As the solution of TBBPA with addition of humic acid was illuminated with LED white light ($\lambda > 400$ nm) in pH 9.0 with air bubbling, TBBPA was obviously degraded (Fig. 1b). The indirect photochemical transformation of TBBPA in aquatic system might occur with ROSs including $\cdot OH$, 1O_2 , $O_2^{\cdot-}$, and H_2O_2 . Therefore, two sets of experiments, ROSs scavenging analysis and ROSs direct detection, were carried out to explore ROSs.

ROSs scavenging analysis. Scavenging experiments were performed using MeOH, FA, NaN_3 , CAT, and SOD to quench $\cdot OH$, e^- and 1O_2 , 1O_2 , H_2O_2 , and $O_2^{\cdot-}$, respectively. The experiment in the presence of N_2 was also examined comparably. That is, before the photochemical degradation experiment, O_2 was removed through 30 min N_2 bubbling. In the experiment, TBBPA exhibited no photochemical degradation with N_2 bubbling but exhibited significant degradation with air bubbling (Fig. 1b). Our data demonstrated that the dissolved O_2 was needed for TBBPA indirect photochemical degradation. When the MeOH (10 mM) was presented in the solution containing humic acid as well as TBBPA under the visible light illumination as a physical trapper of $\cdot OH$, the photochemical degradation efficiencies of TBBPA had no significant change compared with that without adding quenchers (Fig. 2a). Thus, the conclusion drawn that $\cdot OH$ had no notable influence on TBBPA transformation and was not the major ROSs in TBBPA photochemical degradation in this system.

When NaN_3 (10 mM) was added into the solution undergoing irradiation as a physical trapper of 1O_2 , the degradation efficiencies were completely inhibited (Fig. 2a), suggesting that the photochemical degradation of TBBPA indeed involved in the chemical reaction with 1O_2 . Due to TBBPA had no absorption above 350 nm and humic acid had a weak absorption above 400 nm (Fig. S1), 1O_2 was produced from humic acid and subsequently initiated the photochemical reaction of TBBPA. Previous study reported that TBBPA could act as a 1O_2 sensitizer and cause its own degradation

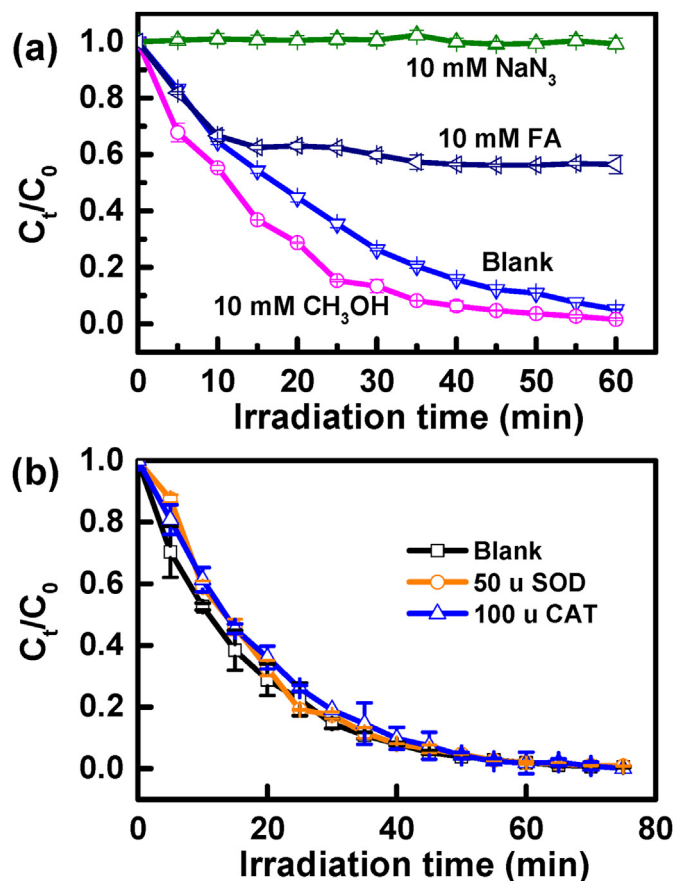


Fig. 2. The photolysis of TBBPA with adding different quenchers (error bars represent standard deviations).

under simulated solar light irradiation (Wang et al., 2015), and humic acid was acted as a precursor or sensitizer for generation of different ROSs (Han et al., 2009). Here, TBBPA had no absorption undergoing irradiation of LED white light, thus $^1\text{O}_2$ was believed to be produced from humic acid. In addition, SOD (50 u) and CAT (1000 u) as a trapper to test this existence and the effect of $\text{O}_2^{\cdot-}$ and H_2O_2 , respectively, were added into the solution, respectively. It was clearly seen that SOD and CAT had no effect on the degradation of TBBPA (Fig. 2b), indicating that both $\text{O}_2^{\cdot-}$ and H_2O_2 were also not involved in TBBPA photochemical reaction in the current system. Therefore, the conclusion can be confirmedly drew that photochemical degradation of TBBPA may be controlled by $^1\text{O}_2$ produced from humic acid under LED white light irradiation.

The detection of ROSs. The ROSs involvement in TBBPA photochemical degradation were also confirmed with the EPR instrument. DMPO and TEMP were employed as probes for $\text{O}_2^{\cdot-}$ and $\cdot\text{OH}$, and $^1\text{O}_2$, respectively. EPR spectrum of the solution with addition to DMPO in the system with TBBPA plus with humic acid did not find the characteristic four-line signal of DMPO- $\cdot\text{OH}$ spin adduct before and after LED white light ($\lambda > 400$ nm) irradiation (Fig. 3a). The results further confirmed that $\cdot\text{OH}$ was not generated in this system under LED white light irradiation. Meanwhile, the characteristic signal of $\text{O}_2^{\cdot-}$ before and after LED white light irradiation was also not observed from the EPR spectrum of methanol containing TBBPA, humic acid, and DMPO (Fig. 3b), indicating that $\text{O}_2^{\cdot-}$ was also not generated in the reaction system. To determine the $^1\text{O}_2$, three characteristic peaks of TEMP- $^1\text{O}_2$ spin adduct could be obtained due to that the three characteristic peaks might be originated from the TEMP itself (Fig. 4a). The intensity signal was

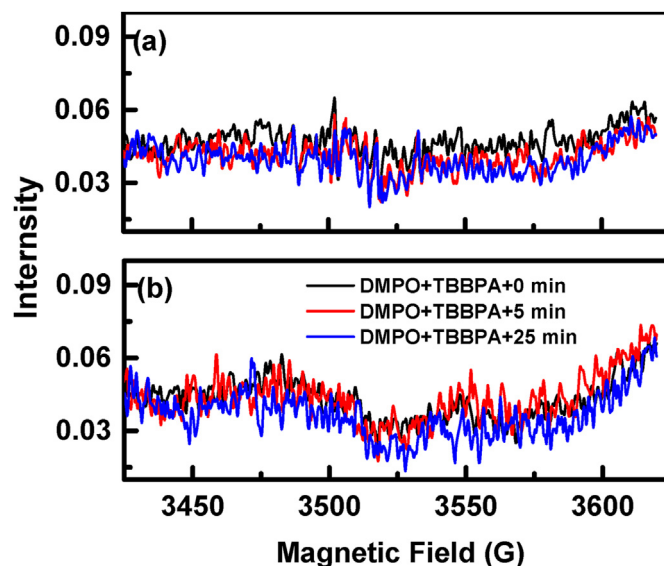


Fig. 3. EPR spectrum of TBBPA (5 mg L^{-1}) and humic acid (0.2 g L^{-1}): (a) in distilled water irradiated ($\lambda > 400$ nm); (b) in methanol irradiated ($\lambda > 400$ nm).

enhanced with addition of humic acid in TBBPA solution (Fig. 4b), while signal intensity decreased with prolonging illumination time from 0 to 25 min (Fig. 4b–d). That is, the signal intensity was higher when TBBPA with humic acid was added than that when TBBPA with humic acid was not added. These results confirmed that $^1\text{O}_2$ was indeed generated in the reaction system under LED white light irradiation.

The humic acid employed in the present work is a natural organic substance originated from the coal. Humic acid was frequently acted as the model compound for environmental dissolved organic matter in water. Illuminated TBBPA with addition of humic acid leading to the production of different ROSs (Fig. 4) which can be inhibited by NaN_3 , a physical quencher of $^1\text{O}_2$. Previous studies showed that humic acid was a relatively weak $^1\text{O}_2$ producer, and $^1\text{O}_2$ photogenerated by humic acid could oxidize halogenated phenols (Canonica et al., 1995; Han et al., 2009). Thus, here, $^1\text{O}_2$ yield from humic acid was a predominant ROS to initiate the rapid photochemical degradation of TBBPA.

Photochemical degradation intermediates and mechanism.

Degradation intermediates were identified using GC/MS first and the relative information is provided in Table 1. Several intermediates would not be determined due to the low level in the system of reaction mixture. However, four intermediates with ring-opening were identified in the present or absent of derivatization, BSTFA:TMCS (99:1, v/v), beside of TBBPA (Figs. S3 and S4). Mass spectra of the four intermediates in Figs. S5–S8 revealed that these four byproducts can be determined with the m/z ($M - 2$): M :($M + 2$) = 1:2:1 isotopic characteristic peak, and the retention times and chemical structures of intermediates as well as TBBPA are summarized in Table 1. Except original compounds A (TBBPA), four intermediates could be authenticated including 2,6-dibromo-4-(propan-2-ylidene) cyclohexa-2,5-dienone (B), 4-(2-hydroxyisopropyl)-2,6-dibromophenol (C), 4-isopropylene-2,6-dibromophenol (D), and 2,6-dibromo-4-(1-methoxy-ethyl)-phenol (E).

To identify more polar intermediates of the TBBPA degradation, we employed HPLC/TOF/MS in this experiment and the information of the obtained intermediates is listed in Table 2. The product 4-(2-hydroxyisopropyl)-2,6-dibromophenol (C) and a hydrolysis debromination product hydroxyl-tribromobisphenol A (F) (The

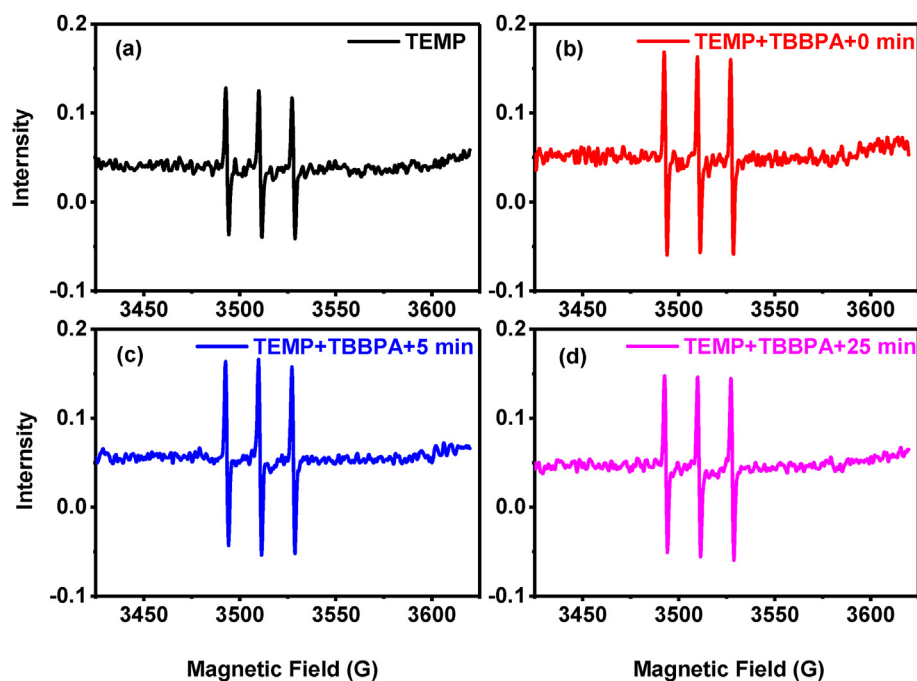


Fig. 4. EPR spectra of TBBPA (5 mg L^{-1}) and humic acid (0.2 g L^{-1}) in distilled water irradiated ($\lambda > 400 \text{ nm}$).

Table 1

Retention time, mass spectra and structure of intermediate products identified by GC/MS.

Compounds [abbreviation]	Rt/min	Chemical structure	m/z of observed fragment ions
A Tetrabromobisphenol A [TBBPA]	32.385		543.8*[M ⁺], 528.8[M ⁺ - CH ₃], 447.8[528.8-Br], 368.9[447.8-Br].
B 2,6-dibromo-4-(propan-2-ylidene)cyclohexa-2,5-dienone	10.859		291.9*[M ⁺], 276.8[291.9-CH ₃], 197.9[276.8-Br].
C 4-(2-hydroxyisopropyl)-2,6-dibromophenol	12.872		309.9*[M ⁺], 294.9[309.9-CH ₃], 278.9[294.9-OH].
D 4-isopropylene-2,6-dibromophenol	13.004		363.9*[M ⁺], 348.9[363.9-CH ₃], 270[348.9-Br].
E 2,6-dibromo-4-(1-methoxy-ethyl)-phenol	14.915		381.9*[M ⁺], 366.9[381.9-CH ₃], 348.9[366.9-OH].

mass spectra are shown in Figs. S9 and S10, respectively) were observed in the indirect photochemical degradation system besides of TBBPA (Fig. S11). Intermediates 4-(2-hydroxyisopropyl)-2,6-dibromophenol (C) and the hydroxyl-tribromobisphenol A (F) were believed as important intermediates in the photochemical degradation. Because the degradation pathways of TBBPA mainly included debromination, hydroxylation and demethylation both by reduction and oxidation reaction system were reported in earlier

studies (Bao and Niu, 2015).

On the basis of detected intermediates by HPLC/TOF/MS as well as GC/MS, the potential degradation pathways could be also suggested (Fig. 5). Three distinct pathways might occur simultaneously in this photochemical process. First, the photochemical degradation of TBBPA happened with addition to the O₂, leading to the generation of intermediates with single aromatic ring, and this process was mainly from the attraction by the ¹O₂ (Fig. 5, Route I). The

Table 2
Retention time, mass spectra and structure of intermediate products identified by HPLC/TOF/MS.

Compounds [abbreviation]	Rt/min	Chemical structure	m/z of observed fragment ions
A Tetrabromobisphenol A [TBBPA]	5.419		542.7452
C 4-(2-hydroxyisopropyl)-2,6-dibromophenol	3.358		308.8939
F [1-(3-bromo-4,5-dihydroxyphenyl)-1-methylethyl]-Phenol	4.622		478.8313

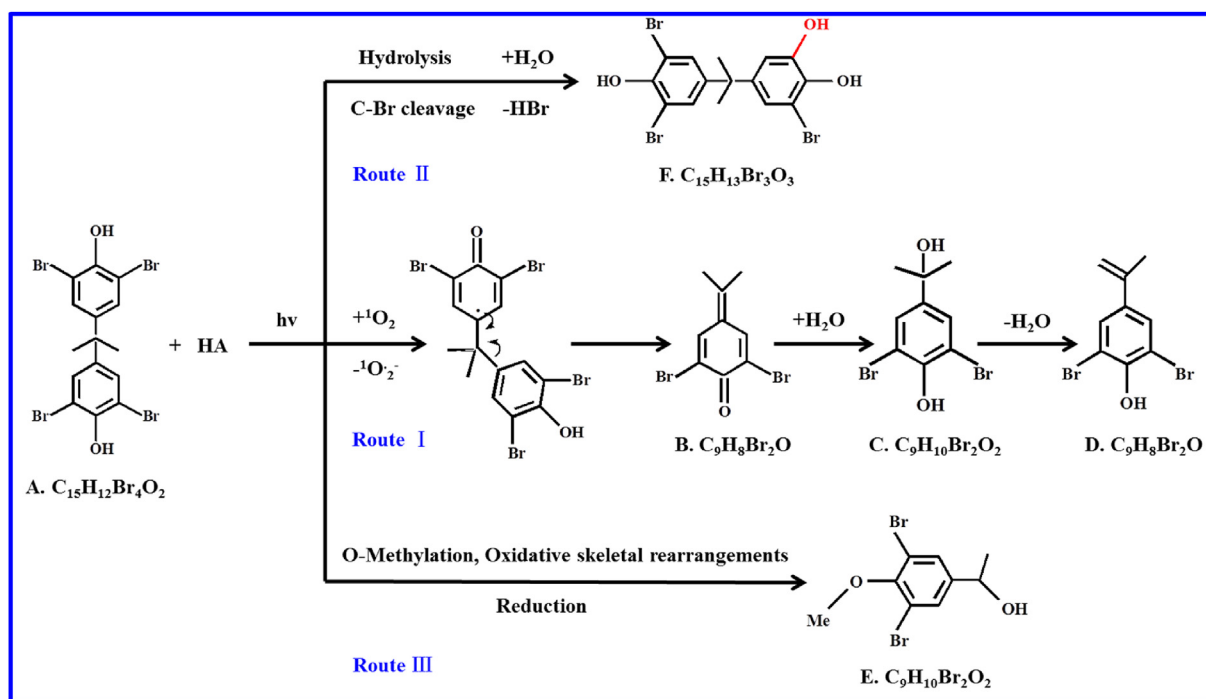


Fig. 5. The proposed degradation pathway of TBBPA in the photolysis process.

reaction of TBBPA with $^1\text{O}_2$ initially generated the phenoxy radicals, and underwent the scission C-C bond as well as the formation of C=C, producing intermediate (B), then was hydrolyzed to produce the intermediate (C) and lost one H_2O molecule to produce the intermediate (D). This reaction pathway was verified and the result was consistent with previous reported studies (Han et al., 2016). On the basis of the identified intermediates (F), hydrolysis debromination pathway was also proposed (Fig. 5, Route II). It is because TBBPA had no absorption under the irradiation of LED white light, the hydrolysis debromination was not the direct photoexcitation product of TBBPA. Humic acid encompassed very diverse structures (Boyle et al., 2009). The contained chromophores can serve as the photosensitizers, either excited directly via the excited states (Canonica et al., 1995; Sul'timova et al., 2008), or excited indirectly via $^1\text{O}_2$ formation (Han et al., 2009). In this work, humic acid absorbed the energy of the photons to produce the excited state, and subsequently quenching the excited singlet as well as the

triplet states by ground state TBBPA. Thus, the hydrolysis debromination was due to the subsequent reaction after photoexcitation of humic acid. In addition, the oxidative skeletal rearrangement pathway was further proposed in the period of the photochemical oxidation of TBBPA with humic acid under irradiation (Fig. 5, Route III). Intermediate (E) would be generated through the reaction of O-methylation, with reduction and oxidative skeletal rearrangement. For the *ipso*-substitution mechanism, the hydroxyl group being attacked at a very rare site connected with a quaternary α -carbon was believed as a well-documented mechanism for TBBPA oxidation in soil slurry and activated sludge (Li et al., 2014, 2015), and the results provided solid evidence that this pathway could also take place during the TBBPA photochemical decomposition process.

3.3. Change of carbon and bromine isotope composition

CSIA could be used to characterize transformation reaction of

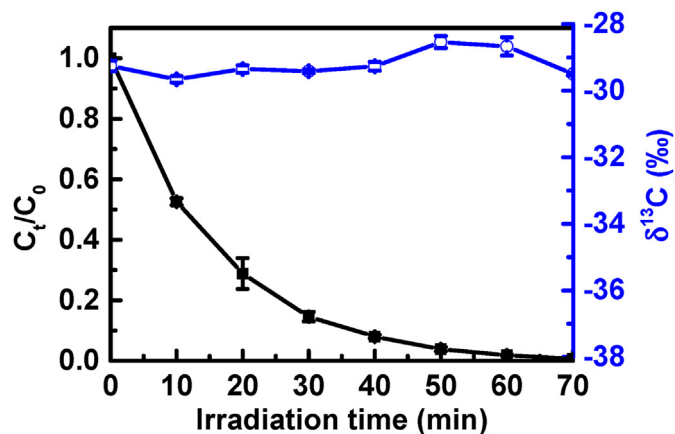


Fig. 6. Isotope fractionation during TBBPA photolysis.

organic pollutants. The fractionation of isotope in the period of photochemical degradation was detected according to the isotope composition of TBBPA at different degradation times. As shown in Fig. 6, no obvious C isotopic fractionation was noticed during the TBBPA photochemical degradation process. No occurrence of any C isotopic fractionation in alkaline solution possibly indicated that the bond cleavage of C-C and C-Br were not the rate controlling step in this process. Because that if the bond cleavage of C-C or C-Br were the rate controlling step of this photochemical degradation, the apparent kinetic isotope effect (AKIE > 1) of normal carbon was anticipated; In this study, the enrichment factor of isotope $\epsilon = 0$ was achieved, and ^{13}C -AKIE = 1 (Eq. (2)) was obtained, indicating that the bond cleavage of C-C and C-Br were not the rate controlling step in this system. In other words, the no fractionation of carbon isotope was observed during the photochemical degradation. Our previous study also showed the no carbon isotopic fractionation prove equally valuable for tracking the source and fate of phenolic brominated flame retardants (Xiong et al., 2015).

The bromine isotopic fractionation during the photochemical degradation process was also attempted in this system. However, due to the inherent physical properties of TBBPA and the instrument restriction of GC/MC/ICPMS, the detection of bromine isotopic fractionation was not achieved completely. However, some previous studies explored the C and Br isotopic fractionation of other brominated organic contaminants in aqueous solution. Zakon et al. investigated C and Br isotopic fractionation of 2-bromophenol and 3-bromophenol during UV-photochemical degradation in aqueous solution. They found that there were also no C and Br isotopic effects observed for 2-bromophenol, while there was Br isotopic effect but no detectable C isotopic fractionation for 3-bromophenol (Zakon et al., 2013). Kozell et al. also explored dual C and Br isotopic effects for tribromoneopentyl alcohol during chemical transformation process, and very small or no statistic difference of Br isotopic fractionation has been probed (Kozell et al., 2015). Furthermore, Bernstein et al. also studied the kinetic bromine isotope effects of brominated phenols and revealed that the values of kinetic isotope effects were also rather low (Bernstein et al., 2013). Above discussion references, we can confirm that the conclusion obtained from this work of no insignificant fractionation of carbon isotope and not detected fractionation of bromine isotope was right and believable.

4. Conclusions

Brominated organic contaminants, such as TBBPA, pose possible risks to aqueous environments. Understanding photochemical

degradation mechanisms, and the change of C and Br isotope effects of TBBPA for the LED white light irradiation system, is a prerequisite for determining the source, behavior and fate of this aquatic micropollutants in a natural environment. Thus, the photochemical degradation of TBBPA in aqueous solution with humic acid took place with LED white light radiation in air bubbling. The results showed that humic acid acted as a weak precursor or sensitizer was one of promising approaches to indirect photochemical degradation of brominated organic contaminants. Four dibrominated intermediates and a hydrolysis debromination product hydroxyl-tribromobisphenol A were identified using GC/MS and HPLC/TOF/MS. Based on these intermediates detected, hydrolysis debromination, reaction induced by singlet oxygen, as well as oxidative skeletal rearrangement were documented as three potential major photochemical degradation routes of TBBPA in this system. The carbon isotope effect analysis demonstrated that no observable carbon isotopic fractionation was observed during photochemical degradation process. No occurrence of isotope effect might be of equal value to exam photochemical degradation process and tracking the source and fate of brominated organic contaminants in the environment.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Jukun Xiong: Methodology, Investigation, Writing - original draft. **Guiying Li:** Writing - review & editing. **Ping'an Peng:** Supervision. **Faina Gelman:** Data curation. **Zeev Ronen:** Validation. **Taicheng An:** Conceptualization, Supervision.

Acknowledgements

This work was supported by National Natural Science Foundation of China (41425015, 41991312, 41703089 and U1901210), Natural Science Foundation of Guangdong Province, China (2017A030310D01) and Leading Scientific, Technical and Innovation Talents of Guangdong special support program (2016TX03Z094). There is no conflict of interests.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2020.127378>.

References

- Aguer, J.P., Tetegan, D., Richard, C., 2005. Humic substances mediated photo-transformation of 2,4,6-trimethylphenol: a catalytic reaction. *Photochem. Photobiol. Sci.* 4, 451–453.
- Amina Si, X., Wu, K., Si, Y., Yousaf, B., 2020. Mechanistic insights into the reactive radicals-assisted degradation of sulfamethoxazole via calcium peroxide activation by manganese-incorporated iron oxide-graphene nanocomposite: formation of radicals and degradation pathway. *Chem. Eng. J.* 384, 123360.
- An, T., Zu, L., Li, G., Wan, S., Mai, B., Wong, P.K., 2011. One-step process for debromination and aerobic mineralization of tetrabromobisphenol-A by a novel *Chrobactrum* sp T isolated from an e-waste recycling site. *Bioresour. Technol.* 102, 9148–9154.
- Bao, Y.P., Niu, J.F., 2015. Photochemical transformation of tetrabromobisphenol A under simulated sunlight irradiation: kinetics, mechanism and influencing factors. *Chemosphere* 134, 550–556.
- Bernstein, A., Ronen, Z., Levin, E., Halicz, L., Gelman, F., 2013. Kinetic bromine isotope effect: example from the microbial debromination of brominated phenols. *Anal. Bioanal. Chem.* 405, 2923–2929.
- Boyle, E.S., Guerriero, N., Thiallet, A., Del Vecchio, R., Blough, N.V., 2009. Optical

- properties of humic substances and CDOM: relation to structure. *Environ. Sci. Technol.* 43 vol 43, pg 2262, 2009 4612–4612.
- Canonica, S., Jans, U., Stemmler, K., Hoigne, J., 1995. Transformation kinetics of phenols in water: photosensitization by dissolved natural organic material and aromatic ketones. *Environ. Sci. Technol.* 29, 1822–1831.
- Chen, N., Wan, Y., Zhan, G., Wang, X., Li, M., Zhang, L., 2020a. Simulated solar light driven roxarsone degradation and arsenic immobilization with hematite and oxalate. *Chem. Eng. J.* 384, 123254.
- Chen, S., Yang, D., Dong, B., Li, N., Dai, X., 2020b. Sludge age impacted the distribution, occurrence state and structure of organic compounds in activated sludge and affected the anaerobic degradability. *Chem. Eng. J.* 384, 123261.
- de Wit, C.A., Herzke, D., Vorkamp, K., 2010. Brominated flame retardants in the Arctic environment - trends and new candidates. *Sci. Total Environ.* 408, 2885–2918.
- Elsner, M., 2010. Stable isotope fractionation to investigate natural transformation mechanisms of organic contaminants: principles, prospects and limitations. *J. Environ. Monit.* 12, 2005–2031.
- Elsner, M., Zwank, L., Hunkeler, D., Schwarzenbach, R.P., 2005. A new concept linking observable stable isotope fractionation to transformation pathways of organic pollutants. *Environ. Sci. Technol.* 39, 6896–6916.
- Fan, M., Zhou, N., Li, P., Chen, L., Chen, Y., Shen, S., Zhu, S., 2017. Anaerobic co-metabolic biodegradation of tetrabromobisphenol A using a bio-electrochemical system. *J. Hazard Mater.* 321, 791–800.
- Fischer, A., Herklotz, I., Herrmann, S., Thullner, M., Weelink, S.A.B., Stams, A.J.M., Schlomann, M., Richnow, H.H., Vogt, C., 2008. Combined carbon and hydrogen isotope fractionation investigations for elucidating benzene biodegradation pathways. *Environ. Sci. Technol.* 42, 4356–4363.
- García-Muñoz, P., Dachtler, W., Altmayer, B., Schulz, R., Robert, D., Seitz, F., Rosenfeldt, R., Keller, N., 2020. Reaction pathways, kinetics and toxicity assessment during the photocatalytic degradation of glyphosate and myclobutanil pesticides: influence of the aqueous matrix. *Chem. Eng. J.* 384, 123315.
- Han, S.K., Sik, R.H., Motten, A.G., Chignell, C.F., Bilski, P.J., 2009. Photosensitized oxidation of tetrabromobisphenol A by humic acid in aqueous solution. *Photochem. Photobiol.* 85, 1299–1305.
- Han, S.K., Yamasaki, T., Yamada, K.-i., 2016. Photodecomposition of tetrabromobisphenol A in aqueous humic acid suspension by irradiation with light of various wavelengths. *Chemosphere* 147, 124–130.
- Howe, P.D., Dobson, S., 2005. 2,4,6-Tribromophenol and other simple brominated phenols. In: *Concise International Chemical Assessment Document*, vol. 66. World Health Organization, Geneva, pp. 1–47.
- Huang, X., Deng, C., Zhuang, G., Lin, J., Xiao, M., 2016. Quantitative analysis of aliphatic amines in urban aerosols based on online derivatization and high performance liquid chromatography. *Environ. Sci.-Proc. Impacts* 18, 796–801.
- Kozell, A., Yecheskel, Y., Balaban, N., Dror, I., Halicz, L., Ronen, Z., Gelman, F., 2015. Application of dual carbon-bromine isotope analysis for investigating abiotic transformations of tribromoneopentyl alcohol (TBNPA). *Environ. Sci. Technol.* 49, 4433–4440.
- Kuemmel, S., Starke, R., Chen, G., Musat, F., Richnow, H.H., Vogt, C., 2016. Hydrogen isotope fractionation as a tool to identify aerobic and anaerobic PAH biodegradation. *Environ. Sci. Technol.* 50, 3091–3100.
- Kuntze, K., Kozell, A., Richnow, H.H., Halicz, L., Nijenhuis, I., Gelman, F., 2016. Dual carbon-bromine stable isotope analysis allows distinguishing transformation pathways of ethylene dibromide. *Environ. Sci. Technol.* 50, 9855–9863.
- Li, F., Jiang, B., Nastold, P., Kolvenbach, B.A., Chen, J., Wang, L., Guo, H., Corvini, P.F.-X., Ji, R., 2015. Enhanced transformation of tetrabromobisphenol A by nitrifiers in nitrifying activated sludge. *Environ. Sci. Technol.* 49, 4283–4292.
- Li, F., Wang, J., Nastold, P., Jiang, B., Sun, F., Zenker, A., Kolvenbach, B.A., Ji, R., François-Xavier Corvini, P., 2014. Fate and metabolism of tetrabromobisphenol A in soil slurries without and with the amendment with the alkylphenol degrading bacterium *Sphingomonas* sp. strain TTNP3. *Environ. Pollut.* 193, 181–188.
- Li, G., Xiong, J., Wong, P.K., An, T., 2016a. Enhancing tetrabromobisphenol A biodegradation in river sediment microcosms and understanding the corresponding microbial community. *Environ. Pollut.* 208, 796–802.
- Li, Y., Li, X., Xiao, Y., Wei, C., Han, D., Huang, W., 2016b. Catalytic debromination of tetrabromobisphenol A by Ni/nZVI bimetallic particles. *Chem. Eng. J.* 284, 1242–1250.
- Maier, M.P., Prasse, C., Pati, S.G., Nitsche, S., Li, Z., Radke, M., Meyer, A., Hofstetter, T.B., Ternes, T.A., Elsner, M., 2016. Exploring trends of C and N isotope fractionation to trace transformation reactions of diclofenac in natural and engineered systems. *Environ. Sci. Technol.* 50, 10933–10942.
- Meckenstock, R.U., Morasch, B., Griebler, C., Richnow, H.H., 2004. Stable isotope fractionation analysis as a tool to monitor biodegradation in contaminated aquifers. *J. Contam. Hydrol.* 75, 215–255.
- Morris, S., Allchin, C.R., Zegers, B.N., Haftka, J.J.H., Boon, J.P., Belpaire, C., Leonards, P.E.G., Van Leeuwen, S.P.J., De Boer, J., 2004. Distribution and fate of HBCD and TBBPA brominated flame retardants in north sea estuaries and aquatic food webs. *Environ. Sci. Technol.* 38, 5497–5504.
- Nakao, T., Akiyama, E., Kakutani, H., Mizuno, A., Aozasa, O., Akai, Y., Ohta, S., 2015. Levels of tetrabromobisphenol A, tribromobisphenol A, dibromobisphenol A, monobromobisphenol A, and bisphenol A in Japanese breast milk. *Chem. Res. Toxicol.* 28, 722–728.
- Passaport, E., Zhang, N., Wu, L., Herrmann, H., Sherwood Lollar, B., Richnow, H.-H., 2018. Aqueous photodegradation of substituted chlorobenzenes: kinetics, carbon isotope fractionation, and reaction mechanisms. *Water Res.* 135, 95–103.
- Reistad, T., Mariussen, E., Fonnum, F., 2005. The effect of a brominated flame retardant, tetrabromobisphenol-A, on free radical formation in human neutrophil granulocytes: the involvement of the MAP kinase pathway and protein kinase C. *Toxicol. Sci.* 83, 89–100.
- Sul'timova, N.B., Levin, P.P., Chaikovskaya, O.N., Sokolova, I.V., 2008. Laser photolysis study of the triplet states of fulvic acids in aqueous solutions. *High Energy Chem.* 42, 464–468.
- Torrentó, C., Palau, J., Rodríguez-Fernández, D., Heckel, B., Meyer, A., Domènech, C., Rosell, M., Soler, A., Elsner, M., Hunkeler, D., 2017. Carbon and chlorine isotope fractionation patterns associated with different engineered chloroform transformation reactions. *Environ. Sci. Technol.* 51, 6174–6184.
- Wang, X., Hu, X., Zhang, H., Chang, F., Luo, Y., 2015. Photolysis kinetics, mechanisms, and pathways of tetrabromobisphenol A in water under simulated solar light irradiation. *Environ. Sci. Technol.* 49, 6683–6690.
- Wiegert, C., Mandalakis, M., Knowles, T., Polymenakou, P.N., Aeppli, C., Machackova, J., Holmstrand, H., Evershed, R.P., Pancost, R.D., Gustafsson, O., 2013. Carbon and chlorine isotope fractionation during microbial degradation of tetra- and trichloroethene. *Environ. Sci. Technol.* 47, 6449–6456.
- Xiong, J., Li, G., An, T., 2015. Development of methodology for the determination of carbon isotope ratios using gas chromatography/combustion/isotope ratio mass spectrometry and applications in the biodegradation of phenolic brominated flame retardants and their degradation products. *Rapid Commun. Mass Spectrom.* 29, 54–60.
- Zakon, Y., Halicz, L., Gelman, F., 2013. Bromine and carbon isotope effects during photolysis of brominated phenols. *Environ. Sci. Technol.* 47, 14147–14153.
- Zhang, T., Liu, Y., Rao, Y., Li, X., Yuan, D., Tang, S., Zhao, Q., 2020. Enhanced photocatalytic activity of TiO₂ with acetylene black and persulfate for degradation of tetracycline hydrochloride under visible light. *Chem. Eng. J.* 384, 123350.
- Zhou, X., Xu, D., Chen, Y., Hu, Y., 2020. Enhanced degradation of triclosan in heterogeneous E-Fenton process with MOF-derived hierarchical Mn/Fe@PC modified cathode. *Chem. Eng. J.* 384, 123324.
- Zu, L., Xiong, J., Li, G., Fang, Y., An, T., 2014. Concurrent degradation of tetrabromobisphenol A by *Ochrobactrum* sp T under aerobic condition and estrogenic transition during these processes. *Ecotoxicol. Environ. Saf.* 104, 220–225.