Photosensitized degradation of 2,4′,5-trichlorobiphenyl (PCB 31) by dissolved organic matter

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ABSTRACT

The presence of dissolved organic matter (DOM) in aquatic system has an important influence on the phototransformation of organic contaminants through the production of reactive substances, such as hydroxyl radicals ($^{\bullet}$OH), singlet oxygen ($^{1}O_2$), and DOM triplet states ($^{3}DOM^{*}$) under solar irradiation. Addition of 5 mg/L of Humic acid sodium (HA), Suwannee River NOM (SRNOM) and Nordic Reservoir NOM (NRNOM) all accelerated the photodegradation of 2,4′,5-trichlorobiphenyl (PCB 31) significantly, with a pseudo-first-order rate constant of 0.0933, 0.0651 and 0.0486 in the initial 12 h, respectively. HA and SRNOM, the allochthonous DOM, showed higher reactivity in the photolysis of PCB 31. The maximum photodegradation rate was observed in 5 mg/L of DOM solution. The roles of the reactive substances were studied by the inhibitory experiments, which suggested that $^{\bullet}$OH and intra-DOM $^{1}O_2$ were more important for the photolysis of PCB 31 than other reactive substances, accounting for 35.1% and 47.1% of the degradation, respectively. The main degradation products of PCB 31 detected by GC–MS were 4-chlorobenzoic acid, 2,5-dichlorobenzoic acid, hydroxy-2,5-dichlorobenzoic acid, 4-hydroxy-2′,5′-dichlorobiphenyls and hydroxy-trichlorobiphenyls. The degradation pathways were accordingly proposed. Photosensitized degradation by DOM, especially the intra-DOM reactions, may be a very important mechanism for the transformation of PCBs and other hydrophobic organic contaminants in the environment.

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1. Introduction

Phototransformation is one of the most important processes that affect the fate and properties of organic compounds in nature. Some of them degrade by absorbing the sunlight directly. For those which do not have absorption in the wavelength range of sunlight, indirect photodegradation in presence of sensitizers is particularly important. Polychlorinated biphenyls (PCBs) widely used as dielectric fluids and flame retardants in electrical capacitors, transformers and plastics [1], are highly toxic and stable chemicals. A large quantity of PCB congeners have been released into the environment causing serious contamination and detrimental effect to the ecosystem [2,3]. Regional contaminations of PCBs in China are usually caused by electronic waste recycling processes, which have presented high risks to local residents and ecosystem [4–6]. There has always been a controversial debate over whether the remediation of PCBs can be processed naturally. PCBs are not easy to be decomposed by biotic pathways and photolysis has been identified as an important process for the attenuation of PCBs. Dechlorination of PCBs under short wavelength (254–300 nm) irradiation in different solvents is well known [7,8]. However, most of the PCB congeners cannot absorb the light above 300 nm [9]. Indirect photodegradation using sunlight and photosensitizers has been proposed for remediation of PCBs. Photosensitizers, such as diethylamine and dyes, absorb light energy and form excited state of molecules and then initiate the dechlorination of PCBs by a photoinduced electron transfer mechanism [9–12].

Dissolved organic matter (DOM) is a heterogeneous mixture of the organic compounds excreted by microorganisms and the breakdown products from decomposing organisms ubiquitous in natural waters [13]. Properties and concentrations of DOM vary greatly among locations, often at concentrations of 0.5–50 mg C/L [14]. The presence of DOM has an important influence on the phototransformation of organic contaminants [15,16]. There is a large quantity of functional groups (chromophores) in the structure of DOM, which can absorb sunlight. Irradiation of DOM can lead to formation of short-lived reactive substances such as hydroxyl radicals ($^{\bullet}$OH), singlet oxygen ($^{1}O_2$), and DOM triplet states ($^{3}DOM^{*}$), peroxyl radicals

($ROO^\bullet$, $O_2^{\bullet-}/HO_2^\bullet$), hydrogen peroxide ($H_2O_2$), hydrated electron ($e_{aq}^-$), and the reactive DOM triplet states ($^3DOM^*$) [17–21], among which $^\bullet OH$, $^1O_2$, and $^3DOM^*$ are particularly important [22]. $^1O_2$ perhaps has the most controversial role, because it can be easily inactivated in aqueous solution by collision with the solvent molecules [23]. The reported concentration of $^1O_2$ measured with the hydrophilic probe (furfuryl alcohol) was also very low [24]. However, the microheterogenous distributions of $^1O_2$ in DOM solutions were demonstrated recently and the apparent concentrations of $^1O_2$ reached 2–3 orders of magnitude higher in the hydrophobic interior of DOM compared with the bulk aqueous phase [25,26]. It is likely that the hydrophobic contaminants (PCBs for example) partitioning into DOM will be exposed to high concentration of $^1O_2$ and be particularly susceptible to photodegradation.

Photosensitized degradation of PCBs by DOM, which might be a very important process for attenuation of PCBs in nature, has been largely overlooked. The objective of the present study was to investigate the photodegradation of one PCB congener (2,4′,5-trichlorobiphenyl, PCB31) sensitized by DOM from different sources under simulated solar irradiation. Roles of reactive substances were studied by adding specific scavengers. The results will help to improve our understanding of phototransformation of PCBs in nature and the potential of using DOM and sunlight for remediation of PCB contaminations.

2. Materials and methods

2.1. Chemicals

2,4′,5-Trichlorobiphenyl (PCB 31), 2,2′,3,3′,4,4′,5,5′,6,6′-decachlorobiphenyl (PCB 209), 2,4,5,6-tetrachloro-m-xylene (TMX) and N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) were purchased from Sigma–Aldrich (Germany). 4-Hydroxy-2′,5′-dichlorobiphenyl was purchased from AccuStandard (US). Humic acid sodium (HA), a natural organic matter sample isolated from coal and often employed as the source of CDOM, was also obtained from Sigma–Aldrich (Germany). The reference DOM, Suwannee River NOM (SRNOM, Product No. 1R101N) and Nordic Reservoir NOM (NRNOM, Product No. 1R108N), were obtained from the International Humic Substances Society (US). DOM was dissolved in water and filtered through the 0.45 μm membrane. Dissolved organic carbon of the store solutions were measured on a TOC-5000 Shimadzu carbon analyzer using KHP standards. 2-propanol and β-carotene were purchased from Sigma–Aldrich (Germany). 2,4,6-trimethylphenol (TMP) and furfuryl alcohol (FFA) were purchased from Alfa Aesar (US). All chemicals and solvents used were of purity at least analytical-reagent grade. Milli-Q water was used whenever required during the experiments.

2.2. Irradiation experiments

The initial concentrations of DOM in the irradiation experiments were 5 mg/L carbon, which was the average value in surface waters [15,30]. The apparent saturated concentrations of PCB 31 in three DOM (5 mg/L) solutions were determined beforehand as the apparent solubility of PCB 31 could be increased by DOM [27], and the lowest value was about 5.0 mg/L. Therefore, 1.0 mg/L was used as the initial concentration of PCB 31 for irradiation. To investigate the influence of DOM concentration on the photodegradation process, different concentrations of HA (1, 5, and 20 mg/L) were used. The roles of different reactive substances in the process were studied by adding 2% (v/v) 2-propanol, 5×10^{-4} mol/L of TMP, 5×10^{-4} mol/L of FFA and 1×10^{-3} mol/L β-carotene into the solution of PCB 31 with 5 mg/L of DOM to scavenge $^\bullet OH$, $^3DOM^*$ (also the formation of $^1O_2$), aqueous $^1O_2$ and intra-DOM $^1O_2$, respectively [28–30]. In order to check the inhibitory effect of chloride ions on the photolysis rate, sodium chloride was added in to the solution of PCB 31 with 5 mg/L of DOM. The original pH of initial test solutions was in range of 7.46–7.95 for the dissolution reason of DOM from different sources. Therefore all solutions were modified to a pH of 7 by adding NaOH (0.1 mol/L) and acetic acid before being put into 25 mL Pyrex (eliminates wavelength below 290 nm) reaction tubes and balanced in dark overnight. A Xutemp XT5409 merry-go-round photochemical reactor (Xutemp Company, Hangzhou, China) with a cooled xenon lamp (1000 W) was used to simulate sunlight. The light intensity (290–420 nm) at the reaction solutions was measured as 0.78 mW/cm^2. Temperature inside the reactor was kept at about $25 °C$. At the meantime light (PCB 31 in water without DOM) and dark (PCB 31 with DOM and no light) samples were also run inside the photochemical reactor. Concentrations of the remaining PCB 31 were analyzed according to the irradiation time. Besides, samples from solutions of PCB 31 with three different DOM (5 mg/L) were collected separately after 36 h of irradiation for analysis of degradation products.

2.3. Analytical determinations

Hexane was used for the extraction of irradiated samples. For PCB 31 analysis, each extract was cleaned up by a Florisil column (Sigma, US) with a top layer of anhydrous sodium sulfate. Then the column was eluted with 100 mL hexane and the eluant was further concentrated to 1 mL. The quantification of PCB 31 was performed by GC-ECD (DB/HP-5 column, Agilent 7890, US). 2,4,5,6-Tetrachloro-m-xylene (TMX) and PCB209 were added to the irradiated samples before extraction processes to detect recoveries [6], and the recoveries were in range of 90–102%.

For analysis of degradation products, the extracts were first applied onto a silica gel column (Sigma, US) with a top layer of anhydrous sodium sulfate. The first fraction eluted with hexane which contained mainly PCB 31 was discarded, and the second fraction eluted with methanol which contained the degradation products was dried completely by a rotary evaporator [31]. BSTFA (0.5 mL) was added to the dried residues and kept at $70 °C$ for 1 h [31]. The TMS derivative solution was then analyzed by a GC–MS instrument (Thermo Fisher Scientific, US) under the scanning mode (50–500 m/z) and selected ion monitoring (SIM) mode. The FTIR spectra (400–4000 cm^{-1}) of three different DOM were determined on a Nicolet Impact 410 FTIR spectrometer (US).

2.4. Statistical analysis

All statistical analyses were performed with Statistical Package for the Social Sciences 16.0 (US) for windows. One-way analysis of variance (ANOVA) was applied to detect significant differences.

3. Results and discussion

3.1. Photodegradation of PCB 31 in DOM solutions

Data of $\ln(C_t/C_0)$ were plotted against irradiation times (Fig. 1), where C_t and C_0 were concentrations of PCB 31 at time t and 0 h, respectively. As shown in Fig. 1, degradations of PCB 31 were all accelerated significantly by addition of 5 mg/L of three different DOM. Direct photolysis of PCB31 in Milli-Q water (without DOM) control experiment was also observed, with an average loss of 16.1% after 36 h of irradiation. No change in PCB 31 concentration was found in the dark controls, indicating that PCB 31 was not degraded by microbes or temperature during the experiments.

The rate data from the initial 12 h of DOM solutions all fitted reasonably well to the pseudo-first-order rate expression (r^2 values were in range of 0.98–0.99). However, the rate constants decreased
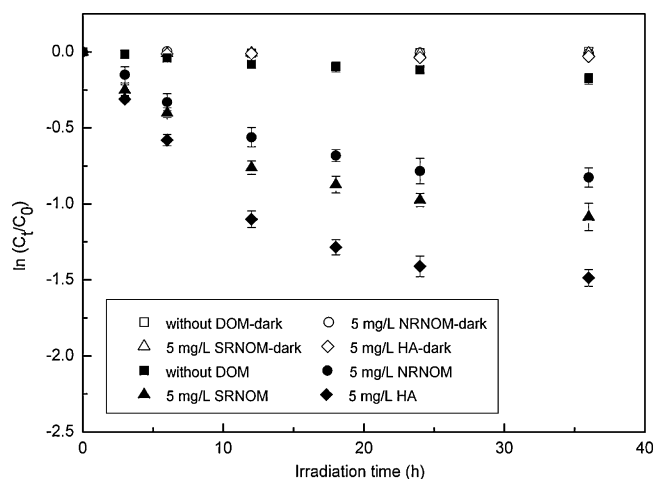
Fig. 1. Photodegradation of PCB 31 in 5 mg/L DOM solutions under simulated sunlight and control conditions. Values represent the mean ± SD of triplicate determinations. C_t and C_0 were concentrations of PCB 31 at time t and 0 h, respectively. HA, Humic acid sodium; SRNOM, Suwannee River NOM; NRNOM, Nordic Reservoir NOM.

Fig. 2. FTIR spectrum of DOM from different sources. NRNOM, Nordic Reservoir NOM; SRNOM, Suwannee River NOM; HA, Humic acid sodium.

afterwards. A quite similar slope of the degradation curves was observed for three different DOM, suggesting that a common inhibition mechanism was involved. One explanation might be the consumption of DOM. It is known that DOM can react with the reactive substances at high rates, which leads to the consumption of chromophores with irradiation time [32,33]. Besides, and the inhibition through interactions between DOM and chloride ions chloride ions have been proved to be able to inhibit the photolysis through the mechanisms of competitive photoabsorption and reactive substances scavenging [34]. It is possible that the chloride ions produced by the oxidation of PCB 31 accumulated with irradiation time and consequently inhibited the photolysis. In order to check the inhibitory effect of accumulated chloride on the photolysis rate, 10 and 100 μM of NaCl were added respectively into the PCB 31 solution with 5 mg/L HA. As shown in Table 1, addition of chloride did not decrease the rate constant obviously, which suggested that the accumulation of chloride was actually not the reason for the inhibition of photolysis after 12 h. Though the photolysis diminished with irradiation time, the photoegradation in the first 12 h was still significant which was important for the attenuation of PCB 31. Therefore, all the rate constants (k_{obs}) and half-lives ($t_{1/2}$) were calculated according to the data from the initial 12 h of the irradiation.

The k_{obs} of PCB 31 in HA, NRNOM and SRNOM from the initial 12 h of irradiation were 0.0933, 0.0651 and 0.0486, respectively. The FTIR results of three DOM from different sources are shown
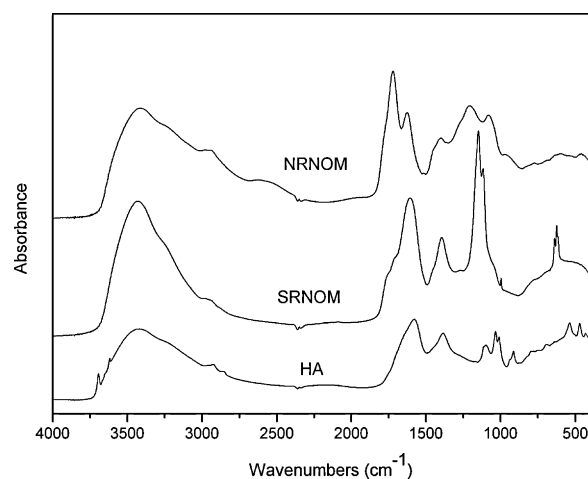
in Fig. 2. The peaks between 3400–3200 cm^{-1}, 1800–1650 cm^{-1} and 1500–1400 cm^{-1} are for –OH stretch, –C=O stretch and COO$^-$, respectively. The peak at around 1050 cm^{-1} might be the Si–O stretch from impurities. Significant compositional variability between DOM of different sources was also revealed by the FTIR spectra, especially in the ranges of 3100–3000 cm^{-1}, 1600–1450 cm^{-1} and 800–680 cm^{-1} which are for aromatic structures. In aquatic systems, the composition of DOM often includes terrestrially (allochthonous) and microbially (autochthonous) derived organic matter. Terrestrial DOM has a higher molecular weight (both number and weight average) distribution and more aromatic moieties than microbially derived DOM [35,36]. Differences in chemical composition can affect the photo-physical and chemical behavior of DOM. The terrestrially derived DOM was reported to show higher absorbance of light per unit carbon [35,37] and a higher yield of •OH production [38] compared with microbially derived DOM. The research of Guerard et al. [39] proved that terrestrial DOM were more reactive than microbially derived DOM in promoting degradation by some reactive oxygen species (ROS) while less reactive in promoting pathways involving ^{3}DOM*. In our study HA, which was isolated from coal, and SRNOM, which was isolated from "black water" were both dominantly comprised of allochthonous materials. NNROM, which was obtained from a drinking water reservoir, was comprised of both allochthonous and autochthonous materials. It was in agreement with the reported studies that the allochthonous DOM-HA and SRNOM showed higher reactivity in the photolysis of PCB 31 than autochthonous DOM-NRNOM.

Table 1

Percent loss of PCB 31 (±S.D.), rate constant (k_{obs}) and half-lives ($t_{1/2}$) in presence of Humic Acid and special scavengers from the initial 12 h of the irradiation.

HA concentration (mg/L) and scavengers[a] (target)/inhibitors	Percent loss (%)[b]	k_{obs} (h^{-1})	$t_{1/2}$ (h)	Inhibition (%)
0	7.87 ± 1.27 a	0.0068	101.9	–
1	47.25 ± 2.04 b	0.0550	12.6	–
5	66.70 ± 1.78 cA	0.0933	7.4	–
20	55.28 ± 2.22 d	0.0692	10.0	–
5 + TMP (^{3}DOM* and ^{1}O$_2$)	28.34 ± 2.90 B	0.0292	23.7	68.7
5 + β-carotene (intra-DOM ^{1}O$_2$)	42.87 ± 1.84 C	0.0494	14.0	47.1
5 + 2-propanol (•OH)	50.65 ± 2.25 D	0.0606	11.4	35.1
5 + FFA (aqueous ^{1}O$_2$)	62.08 ± 1.42 E	0.0817	8.5	12.4
5 + 10 μM NaCl	69.27 ± 1.06 A	0.0978	7.1	−4.82
5 + 100 μM NaCl	64.83 ± 2.42 A	0.0913	7.6	2.11

[a] TMP: 2,4,6-trimethylphenol; FFA, furfuryl alcohol.
[b] Different lowercase letters (a, b, c, and d) indicate significant ($p < 0.01$) difference between treatments with different concentrations of HA. Different capital letters (A, B, C, D, and E) indicate significant ($p < 0.01$) difference between treatments with different/no scavengers.

Table 2
Mass spectra data (m/z) of degradation products of PCB 31 with BSTFA derivatization detected by GC/MS.

Products	Rt (min)	Characteristic ions (m/z)			
4-Chlorobenzoic acid	9.54	228(M^+)	213 (M^+–CH_3)	184 (M^+ –COO)	111 (M^+–TMS –COO)
2,5-Dichlorobenzoic acid	11.31	262 (M^+)	247 (M^+–CH_3)	173 (M^+–TMS–O)	145 (M^+–TMS–COO)
OH-dichlorobenzoic acid	17.31	350 (M^+)	335 (M^+–CH_3)	306 (M^+ –COO)	198 (M^+–TMS–COO–Cl)
4-OH-2′,5′-diCB	18.01	310 (M^+)	295 (M^+–CH_3)	259 (M^+–CH_3–HCl)	243 (M^+–CH_3–HCl–O)
OH-triCB	19.45	344 (M^+)	329 (M^+–CH_3)	293 (M^+–CH_3–HCl)	277 (M^+–CH_3–HCl–O)

3.2. Effect of DOM concentration on PCB 31 photodegradation

The rate data from the initial 12 h of PCB 31 solutions with HA of different concentrations all fitted well to the pseudo-first-order rate expression (r^2 values were in range of 0.96–0.99). The amphoteric effects of DOM on the phototransformation of organic pollutants have been observed in many studies [9,30,40]. The proposed mechanisms for the decrease in phototransformation often involved the scavenging of reactive substances [32], light attenuation [9] and reduction of oxidation intermediates [41]. As shown in Table 1, increased DOM concentration from 0 to 5 mg/L accelerated the photoegradation significantly but decreased the rate constant when it reached to 20 mg/L. Given that the average concentration of DOM in fresh waters is between 5.0 and 10.0 mg/L [13], the

photodegradation of PCB 31 in fresh waters is likely occurring at a maximum rate, which shows great impact on the fate of PCB 31 in the environment.

3.3. Roles of the reactive substances

The data of $\ln(C_t/C_0)$ from the initial 12 h photodegradation of PCB 31 in presence of 5 mg/L HA together with various scavengers were also plotted against irradiation times. All the rate data fitted reasonably well to the pseudo-first-order rate expression (r^2 values ranged from 0.97 to 0.99) and the rate constants were subsequently calculated (Table 1).

The addition of 2-propanol decreased the rate constant by 35.1%. It is well known that 2-propanol predominantly scavenge •OH to
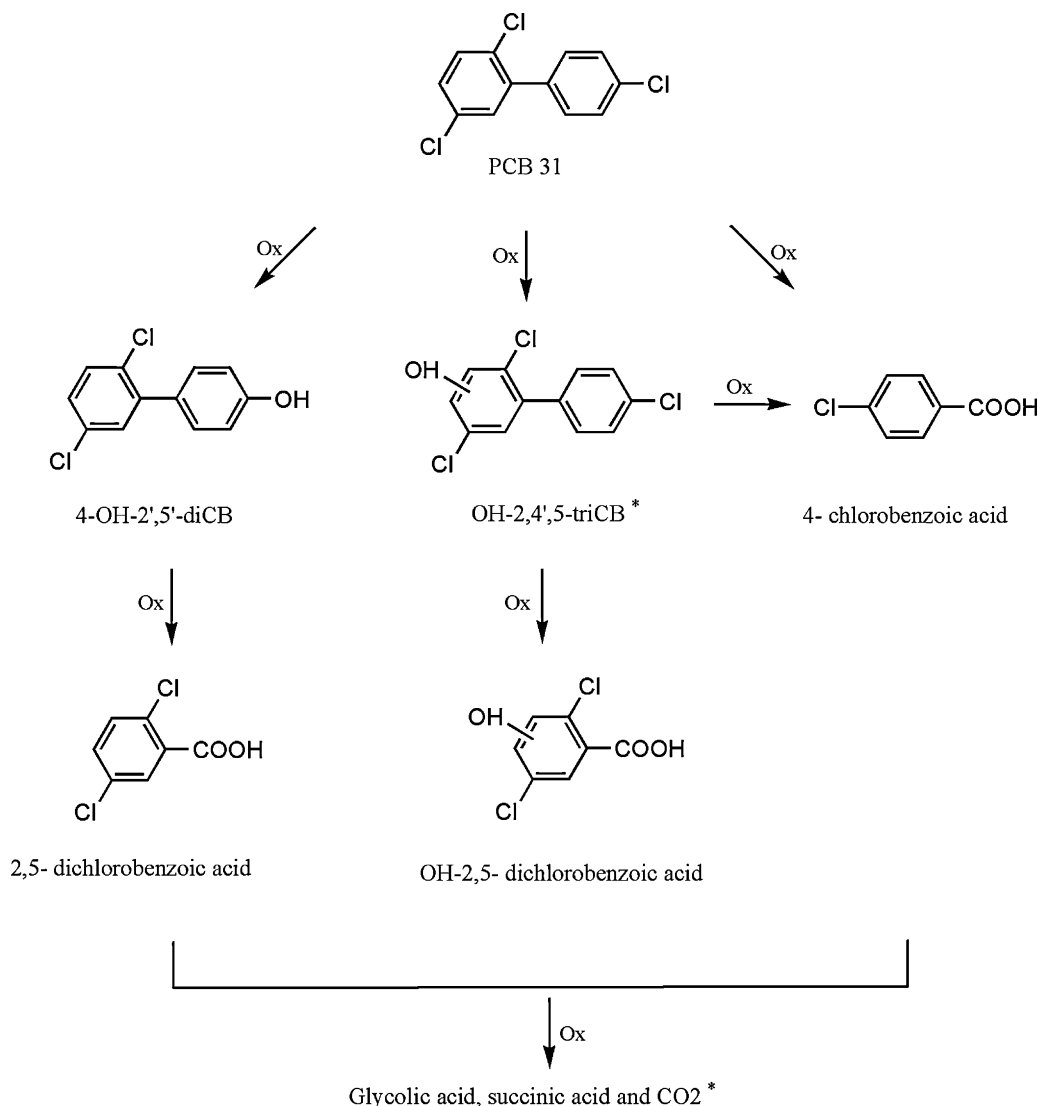

Fig. 3. Proposed photodegradation pathways of PCB 31 in DOM solutions. *The chemical structures were estimated from the progress of degradation pathways.

other reactive substances [42]. 0.5% (v/v) 2-propanol was proved to completely inhibit the photoreaction of 4-nitropyrocatechol with •OH in 10.0 to 100 mg/L humic acid solutions. Therefore, 2% (v/v) 2-propanol used in this study was sufficient to inhibit the reaction of •OH with PCB 31. Furfuryl alcohol (FFA) was used as the special scavenger of $^1O_2$ in the bulk solution for its well known rose bengal-sensitized photooxygenation ($k = 1.2 \times 10^8$ m^{-1} s^{-1}) with a yield of 85% [43]. FFA is a hydrophilic scavenger and only reacts with the $^1O_2$ in aqueous phase, while β-carotene has been suggested as an effective hydrophobic scavenger to inhibit the intra-DOM reactions [28], for example the reactions of $^1O_2$ with PCB 31 in the hydrophobic microregion. According to Table 1, the rate constant was decreased by 12.4% and 47.1% in presence of FFA and β-carotene, respectively. The addition of TMP decreased the rate constant by 68.7%. TMP was said to be able to react with $^3DOM*$ and $^1O_2$ at a high rate [24,29,44]. $^3DOM*$ is formed by inter-system crossing after the radiation absorption of DOM and reactions between $^3DOM*$ and fundamental-state triplet oxygen lead to the production of $^1O_2$ [45]. Thus the addition of TMP in the experiment inhibited the reactions of PCB 31 with both $^3DOM*$ and $^1O_2$. Direct reactions of $^3DOM*$ with organic compounds have been proved by recent studies [16,39]. The contribution of $^3DOM*$ to the degradation of PCB 31 via direct energy transfer was calculated as 9.2%. Results of the inhibitory experiments indicated that •OH and intra-DOM $^1O_2$ were more important for the photolysis of PCB 31 in DOM solutions compared with aqueous $^1O_2$ and $^3DOM*$, accounting for 82.2% of the degradation in all.

3.4. Photodegradation products and proposed pathways

The main products from photolysis of PCB31 in presence of three DOM (5 mg/L) after 36 h of irradiation were decided according to the spectral data of the products and the reference compounds obtained by GC/MS and were quite similar, which were 4-chlorobenzoic acid, 2,5-dichlorobenzoic acid, hydroxy-2,5-dichlorobenzoic acid, 4-hydroxy-2′,5′-dichlorobiphenyls and hydroxy-trichlorobiphenyls. Mass spectral data of the main products are listed in Table 2. The GC/MS spectra of the products and one example of the mass spectrum of one product (Rt 11.31 min) from the irradiated PCB 31 solution with 5 mg/L HA are shown in the supplementary material (Figs. S1 and S2). Because some of the reference compounds for OH-triCB were not available, the exact chemical structures were unknown. However, it has been reported that the *para*-positions were the most likely sites of attack by •OH based on the calculated electric charge distribution and frontier electron density on carbon atoms [31]. Besides, OH-2,5-dichlorobenzoic acid was detected as one of the products. Therefore the structure for OH-triCB could be inferred accordingly. The final oxidation products of PCBs reactive species such as •OH were reported to be glycolic acid, succinic acid or even CO$_2$ [31,46]. However, they were not detected in the present study, perhaps for their low concentrations. Dihydroxy-trichlorobiphenyls and dihydroxy-dichlorobiphenyls which were supposed to be produced [31,47] were not detected either. The explanation might be that the dihydroxy-PCBs could be oxidized into quinones which subsequently reacted with the active functional groups in DOM structure, for example the nitrogen and sulfur nucleophilic groups, to form adduct which could not be detected by GC/MS [48]. The photodegradation pathways of PCB 31 in DOM solutions were proposed according to the main products (Fig. 3), where glycolic acid, succinic acid and CO$_2$ were assumed to be the major products in the last stage of photodegradation.

4. Conclusions

Addition of HA, NRNOM and SRNOM all accelerated the photodegradation of PCB 31 significantly, with a pseudo-first-order rate constant of 0.0933, 0.0651 and 0.0486 in the initial 12 h at 5 mg/L, respectively. Though the photolysis diminished with irradiation time, the photodegradation of PCB 31 in the initial 12 h was still of great significance, which might be important for the attenuation of PCB 31 in nature. DOM from various sources presented different photochemical reactivity. HA and SRNOM, which were dominantly allochthonous DOM showed higher reactivity in the photolysis of PCB 31 than autochthonous DOM-NRNOM. The concentration of DOM had amphoteric effects on the phototransformation of PCB 31 and the maximum rate was observed in DOM solution of 5 mg/L. Several reactive substances such as $^3DOM*$, $^1O_2$ and •OH were involved in the indirect photolysis of PCB 31 in DOM solutions. Results of the inhibitory experiments suggested that •OH and intra-DOM $^1O_2$ were more important for the phototransformation of PCB 31, accounting for 35.1% and 47.1% of the degradation, respectively. The aqueous $^1O_2$ and $^3DOM*$ accounting for 21.6% of the degradation in all were less important. Photolysis of PCB31 sensitized by DOM produced 4-chlorobenzoic acid, 2,5-dichlorobenzoic acid, hydroxy-2,5-dichlorobenzoic acid, 4-hydroxy-2′,5′-dichlorobiphenyls and hydroxy-trichlorobiphenyls as the main products. The degradation pathways were accordingly proposed and it will help to improve our understanding of phototransformation of PCBs. Hydrophobic organic contaminants are likely to bind with DOM, which brings the hydrophobe into a hydrophobic microregion with much higher concentrations of reactive species. Indirect photolysis in presence of DOM, especially the intra-DOM reaction, may be a very important mechanism for the transformation of hydrophobic organic contaminants like PCBs, DDT and so on in the environment. Photosensitized degradation by DOM also provides a promising method for the remediation of regional contamination of PCBs.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.10.061.

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