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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 ($^1O_2$), 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 $^1O_2$ 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.

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 ($^1O_2$), and DOM triplet states (^{3}DOM*), peroxyl radicals

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($ROO^\bullet$, $O_2^{\bullet -}/HO_2^\bullet$), 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