

A simulation research on the natural degradation process of tetrabromobisphenol A in soil under the atmospheric different environments

Chen Liu^{1,2,3} · Xiaojun Niu^{1,2,3,4} · Xiaofei Song^{1,2}

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Abstract Tetrabromobisphenol A (TBBPA) is one of the most commonly used flame retardants and has become an environmental contaminant worldwide. More data on the basic characteristics of TBBPA are needed to better understand and used to describe its environmental fate. The aim of this study is to investigate the degradation of TBBPA with different degrees of bromination under the atmospheric different environments. TBBPA was removed quickly due to the strong oxidizing ability of ozone in the atmospheric environment. The half-life of TBBPA was approximately 2.5 h when the ozone concentration was 0.3 mg L^{-1} . The degradation reaction rates of TBBPA increase with increasing ozone concentration but decreased with increasing soil depth. When the ozone concentration was 10 mg L^{-1} , the removal rate of TBBPA reached 90.37 % at the soil surface after 2 h. Under UV irradiation, TBBPA was removed quickly, and the photodegradation reactions were faster than with solar irradiation. The conditions of alkaline soil and high ground

temperature in the summer were both contributors to the degradation of TBBPA. These results could facilitate the improvement of waste treatment designs and could lead to better predictions of the outcome of TBBPA in the environment.

Keywords TBBPA · Degradation · Ozone · Irradiation · Temperature · pH

Introduction

Tetrabromobisphenol A (TBBPA; 4,4'-isopropylidenebis(2,6-dibromophenol) is one of the brominated flame retardants (BFRs) used in electronic industrial applications commonly and is preferred over other BFRs in manufacturing operations (George and Häggblom 2008; Voordeckers et al. 2002). On account of its widely used, TBBPA has turned into a universal environmental contaminant and has been detected in the environment, biota, and human body (Zhang et al. 2009; Sjödin et al. 1999; de Wit et al. 2006). Numerous studies have shown negative physiological effects of TBBPA, and its toxicity to human and organism has been paid increasing attention (Hakk and Letcher 2003; Covaci et al. 2009). Virulence of TBBPA to mammals is indicated to be low; however, TBBPA is fatal to aquatic organisms such as fish and algae at low concentrations (Damerud 2003). More electronic waste (e-waste) recycling is currently performed in China than in any other part of the world. It is estimated that about 90 % of the worldwide e-waste imported into Asia, which imported into China in the legal or illegal forms (Chen et al. 2009). Low labor costs and weak environmental regulations and enforcement result in primitive e-waste recycling techniques, including manual dismantling, which were widely used from the 1990s to the early 2000s; these processes led to large quantities of toxic metals

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✉ Xiaojun Niu
xjniu@scut.edu.cn

¹ College of Environment and Energy, South China University of Technology, Guangzhou 510006, PR China

² The Key Lab of Pollution Control and Ecosystem Restoration in Industry Clusters, Ministry of Education, Guangzhou, People's Republic of China

³ The Key Laboratory of Environmental Protection and Eco-Remediation of Guangdong Regular Higher Education Institutions, Guangzhou 510006, People's Republic of China

⁴ State Key Laboratory of Subtropical Building Science, South China University of Technology, Guangzhou, Guangdong 510640, People's Republic of China

and organic pollutants released into the surrounding environment (Luo et al. 2011; Wang et al. 2011).

With the rapid development of synthetic materials, TBBPA is mainly employed in the preparation of epoxy resin, alkyne resin, butadiene phenyl ethyl resin (ABS), and polystyrene (PVC), which are used in the manufacture of printed circuit boards. This has given rise to a dramatic increase in TBBPA production (BSEF 2006). Fackler (1989) has suggested that the half-life of TBBPA is approximately 2 months through conducted biodegradation studies in several media (soil, river sediment, and water). In contrast, there was no degradation observed in sludge under sewage treatment conditions (Anonymous 1992). TBBPA is a kind of potential environment endocrine interference, similar with persistent organic pollutants (POPs). It can accumulate in the environment and biota and have serious influence to the environment and the living creature (Thomsen et al. 2001; Watanabe and Sakai 2003; Berger et al. 2004; Morris et al. 2004). However, there has been little research on the concentration of TBBPA in soils from e-waste recycling areas in China, and in particular, there has been little research on its natural degradation in soils. Bisphenol A, the final reductive debromination product of TBBPA, is known to show estrogenic activity (Huang et al. 2012; Renner 1997), and its fate in soils remains to be elucidated.

Soil is a receptor for gaseous pollutants or particulate forms that are emitted from e-waste recycling. Under present circumstances, TBBPA has the largest production volume (50 % of the BFRs in current use) (Hornung et al. 2003; BSEF 2003), which makes it significant to understand its degradation processes and fate in the soil environment. According to previous reports, the reductive dehalogenation of highly halogenated compounds is a key step in its degradation in the environment. TBBPA has been found to be reductively dehalogenated and then to be further degraded by microorganisms (Arbeli and Ronen 2003; Ronen and Abeliovich 2000). Biogeochemical process and remediation research have only recently started to be conducted on BFRs in soil in China (Liu et al. 2013), in spite of the fact that BFRs have been discharged from e-waste recycling activities into the environment for more than 20 years (Chen et al. 2009; Luo et al. 2011; Wang et al. 2011; Wong et al. 2007). However, the ozone decomposition and the effect of photolytic factors, which are changed by the atmospheric environment through the degradation reaction of TBBPA, are not well documented.

The majority of past literature reviews discussed contaminants individually, and only a few studies associated the changes of the atmospheric environment with the natural degradation process of TBBPA. In recent years, air pollution has caused the concentrations of atmospheric O₃, CO₂, SO₂, and other harmful gases to increase rapidly, contributing to the acceleration of global warming. Furthermore, the phenomenon of gradual ozone depletion has aroused great concern

(Yang 2012), as the destruction of the ozone layer will lead to excessive ultraviolet radiation reaching the ground. In addition, the increase in the frequency of acid rain maintains a stable distribution area, but in south China, especially in the Pearl River Delta region, the phenomenon of acid rain is more serious (Zhi et al. 2011). Through correlation analysis between the atmospheric environment and the natural degradation process of volatile and semivolatile organic compounds, the identification of certain pollutants from different recycling activities and nature environment can be clarified and better achieved, along with identifying changes in the atmospheric environment.

The objectives of this study, therefore, are to (1) perform degradation experiments on TBBPA to understand debromination trends under different ozone concentrations, (2) explore the difference between UV lamp irradiation and solar light in the degradation process of TBBPA, (3) determine the time course of degradation and evaluate of photodegradation efficiency of TBBPA under different light intensities, and (4) vary the exposure temperature and soil pH to evaluate the natural degradation characteristics of TBBPA, as a basis to infer the contribution of changes in the natural environment to the degradation of TBBPA in the soil of the e-waste dismantling areas.

Materials and methods

Materials

TBBPAs, the purity >98 %, were purchased from AccuStandard Inc. (CT, USA). A stock standard solution of the TBBPA was prepared by adding 1 mL of purchased TBBPA into 1 mL of isooctane and was stored in opaque bottles at −20 °C. Silica gel (100–200 mesh) and alumina (100–200 mesh) were extracted by using Soxhlet extraction with methanol for 24 h and then with dichloromethane for another 24 h. Silica gel and alumina were then activated at 180 and 250 °C for 12 h, respectively, and deactivated with distilled water (3 %, w/w) prior to use. All of the organic solvents were redistilled by using a glass system.

Sample preparation

In accordance with the average TBBPA pollution levels of the e-waste dismantling areas in the soil of south China (Huang et al. 2014), this experimental design entailed weighing 0.1 mg of TBBPA flame retardants and adding it to 1 L of hexane (TBBPAs were not detected) dissolved in 1 kg of soil collected from a grassland beside the College Environment and Energy Building at South China University of Technology, Guangzhou, Guangdong (23° 02' 47" N, 113° 24' 08" E) with no sources of pollution. The clean soil samples

were found to not be contaminated by TBBPA and treated with high-temperature steam produced by the autoclave for sterilization. After that, all the soil samples were freeze-dried, ground, and homogenized by sieving through an 80-mesh stainless steel sieve, stored in aluminum foil at $-4\text{ }^{\circ}\text{C}$. The initial concentration of TBBPA was $0.1\text{ }\mu\text{g g}^{-1}$. The contaminated soil was then stirred with a stirring mixer for 24 h, transferred to brown glassware to be shaken for 24 h, and finally cultured for 2 days under natural conditions to allow for the adsorption equilibrium of TBBPA to be achieved in soil. All of the samples were stored at $-4\text{ }^{\circ}\text{C}$ until analysis was conducted. Except the temperature experiments, the identical operational conditions of all experiments were conducted under room temperature $25\text{ }^{\circ}\text{C}$, and except the pH experiments, the pH of soil samples stay around 7.58.

Extraction and cleanup

The extraction method was adapted from a procedure developed in our laboratory for the analysis of persistent organic pollutants in soil (Niu et al. 2015). Blank soil samples (1 g) were extracted by ultrasonic extraction using a mixture of 60 mL of acetone and *n*-hexane (1:1, *v:v*) for 30 min. The extracts were concentrated to 2 mL using a rotary evaporator and then purified and fractionated using a glass column packed with silica gel/alumina.

The silica/alumina column was packed from bottom to top with neutral alumina (6 cm, 3 % deactivated, *w:w*), neutral silica gel (2 cm, 3 % deactivated, *w:w*), 33 % sodium hydroxide silica (5 cm), neutral silica gel (2 cm, 3 % deactivated, *w:w*), and 44 % sulfuric acid silica (8 cm). The TBBPA mixture was eluted with 70 mL of hexane:dichloromethane (1:1, *v:v*), and this eluent was concentrated using rotary evaporation and further reduced with a gentle N_2 stream to a final volume of 200 μL . A known amount of standard was added to the extracts prior to instrumental analysis.

Derivatization

Derivatization is indispensable to improve the chromatographic peaks of the highly polar TBBPA. An aliquot (100 μL) of each standard or extract solution was transferred into a 2-mL reaction vial, and 50 μL of BSTFA containing 1 % TMCS was added. The vial was then filled with N_2 , closed, and left for 30 min at $60\text{ }^{\circ}\text{C}$. Finally, an aliquot (5 μL) of the solution was analyzed by GC-MS.

Measurement and identification of products

An Agilent GC 7890A equipped with a 7683B Series Injector and interfaced with a mass spectrum Agilent 5795C (Agilent, USA) and operated in electron impact ionization (70-eV electron energy) was utilized to monitor the degradation of

TBBPA and to identify the reaction products. A 30-m HP-5MS capillary column (0.25 mm i.d., 0.25- μm film thickness) was used for separation. Helium gas (1.0 mL min^{-1}) was used as the carrier gas. A 5 μL sample was introduced into GC in splitless mode. The injection port temperature was $280\text{ }^{\circ}\text{C}$. The initial oven temperature was $100\text{ }^{\circ}\text{C}$ for 1 min. The temperature was then increased by $20\text{ }^{\circ}\text{C min}^{-1}$ to $210\text{ }^{\circ}\text{C}$, then by $4\text{ }^{\circ}\text{C min}^{-1}$ to $250\text{ }^{\circ}\text{C}$, and finally by $2\text{ }^{\circ}\text{C min}^{-1}$ to $290\text{ }^{\circ}\text{C}$ for 5 min. The MSD was operated in full scan mode with a scanning range of 50–900 *m/z*. The quantification of identified degradation products was acquired in selected ion monitoring (SIM) mode with external calibration curves. Data acquisition began after a solvent delay of 5 min. The quadrupole temperature and ion source temperatures were set at 230 and $150\text{ }^{\circ}\text{C}$, respectively.

The identification of the different congeners in the samples was based on comparison of their MS data and retention times with those of authentic reference standards and those reported in the literature.

Quality control and assurance

To prevent any possible photolysis of TBBPA analytes, special care was taken to avoid the exposure of samples to light during their storage and analysis. All of the sample preparation and treatment were conducted under reduced light conditions, and all of the glasswares were wrapped in aluminum foil.

For instrumental quality control, the blank soil samples were spiked with a standard solution of TBBPA, then extracted by the pretreatment method. Recoveries of TBBPA were obtained by GC-MS and in the range of 82–95 % for the soil samples. The analyzed concentrations were corrected for the recovery rate. A procedure blank control was included for each set of five soil samples, and all of the blank controls contained no detectable amounts of the target substances. Quantification was performed using an internal calibration method (more than five concentration levels). No target BFRs were detected in the method and solvent blanks; therefore, the limit of detection (LOD) was calculated by extrapolating the concentration that would give a signal-to-noise ratio of 3 ($S/N=3$) by injecting an extracted spiked sample of the lowest concentration. The method LOD was 3 ng g^{-1} for TBBPA of soil samples (assuming a sample mass of 1 g). Samples with concentrations below the detection limits were expressed as non-detected (nd) and calculated as zero. TBBPA was expressed as milligrams per gram of dry weight (dw) in the soil samples.

Ozone experiments

The ozone degradation experiments were performed in the laboratory with an ozone generator. The whole process of

the ozone experiments was conducted under room temperature 25 °C and kept in dark environment to avoid photodegradation; the pH of soil samples stay around 7.58, and the sterilization was applied to avoid microorganism degradation. These experiments were equipped with two different sizes of column soil reactor to study the effect of ozone concentration, flow time, and soil depth on the degradation of TBBPA. The ozone experiment was divided into two series; the first series utilized a low ozone concentration based on the average atmospheric ozone concentration in south China (Yang 2012), and the second series involved the use of high ozone concentrations. In the first series, the soil sample was packed into a column with a length of 15 cm, a diameter of 100 mm with an ozone concentration of 0.3 mg L (g)⁻¹, and a flow rate 100 mL min⁻¹ was used. The column was run for 256 h with soil samples taken at 2, 4, 8, 16, 32, 64, 128, and 256 h at different depths to analyze the degradation-generating TBBPA concentrations. In the second series (high concentration ozone series), the soil sample was packed into a 15-cm column with a diameter of 40 mm with five different ozone concentrations consisting of 1, 3, 5, 7.5, and 10 mg L (g)⁻¹, and a flow rate 100 mL min⁻¹ was used. Each column was run for 2 h, and soil samples were taken from the column at different depths to analyze the concentrations of degradation-generating TBBPA.

Irradiation experiments

UV exposure experiments were conducted both under natural conditions with outdoor sunlight and in the laboratory with artificial UV light. The temperature was measured regularly in both experimental setups and was never found to exceed 28 °C outdoors or 25 °C indoors. The pH of all the soil samples stay around 7.58, and the sterilization was applied to exclude the biodegradation.

Each experiment consisted of blank soils, control samples kept in the dark and to be exposed during the experiment. All of the experiments were performed in triplicate. The laboratory exposure light source composed of one 16-W mercury UV lamp and equipped with filters to give a spectrum approach to sunlight in the UV-A range (300–400 nm) (Shih and Wang 2009). The intensity of irradiance at the exposure spot was 1.0 mW cm⁻² from the UV lamps. Soil samples were transported to a photochemical setup equipped with mercury UV lamps in a hood for the indoor experiments, and soil samples were collected at various time points between 0 and 256 h. Sunlight exposure experiments were conducted from 24 February to 15 April 2014 on the roof of the College Environment and Energy Building at South China University of Technology, Guangzhou, Guangdong. The setup was placed in direct sunlight on a roof for the outdoor experiments and also sampled at various time points between 0 and 256 h. The weather conditions during the sunlight

exposure experiments were excellent with clear skies. Maximum UV irradiance was 1.0 mW cm⁻² from the sun at midday. A comparison between indoor and outdoor irradiation can be seen in Fig. 4. Irradiance from a 24-h cycle of sunlight was found to correspond to approximately 8 h of artificial UV light in this experiment. All samples were stored in the dark before and after exposure.

Temperature and pH experiments

A certain amount of samples were transported to two incubators with different temperatures. The temperature of the one incubator was set at 25 °C based on the average room temperature in south China, and the temperature of the second incubator was set at 40 °C, corresponding to the maximum ground temperature in the summer in south China (Ding et al. 2011; Chen and Guo 2012). Periodic sampling was then used to complete the measurements.

In accordance with the protocol proposed by Zhi et al. (2011), a particular amount of samples was weighed and placed in another incubator, which also set to room temperature (25 °C). The pH of the sample in each petri dish was set to approximately 2.0, 5.0, and 9.0, respectively. Periodic sampling was then conducted in the measurements.

The temperature and pH experiments were both conducted in the dark environment to avoid photodegradation. Except the temperature experiments, the identical operational conditions of all experiments were conducted under room temperature 25 °C, and except the pH experiments, the pH of soil samples stay around 7.58.

Additionally, all experiments of this study are based on single-factor experiment; the control treatment was one set of the temperature experiments. This control treatment was conducted in the dark environment to avoid photodegradation; under room temperature 25 °C, the pH of soil samples stay around 7.58 and the sterilization was applied to exclude the biodegradation. The result of control treatment of this study is shown in Fig. 5.

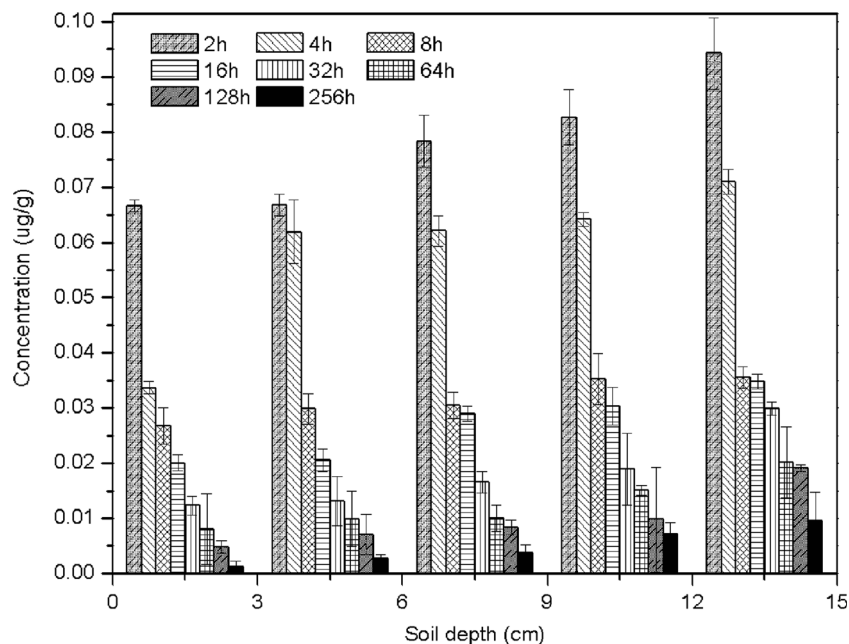
Results and discussion

TBBPA degradation in soil of different depths under low ozone concentration

Because the ozone concentration and soil depth could be important parameters in controlling the TBBPA degradation process, the effect of the degradation rate of TBBPA in indoor simulated experiments under low concentrations of ozone (0.3 mg L⁻¹) in soil was investigated over the depth range of 1 to 15 cm over 256 h.

Figure 1 shows that the percentage of TBBPA noticeably decreased by increasing the ozone flow time. After ozone was

Fig. 1 The concentrations of TBBPA under low ozone conditions at soil depths of 0–3, 4–6, 7–9, 10–12, and 13–15 cm. Soil samples were taken at 2, 4, 8, 16, 32, 64, 128, and 256 h



forced into the soil columnar reactor for 2, 4, 8, 16, 32, 64, 128, and 256 h, the percentage of TBBPA was 66.63, 33.7, 26.8, 20.08, 12.35, 8.01, 4.8, and 1.14 % on 1–3-cm surface soil, respectively. During each period, the average removal rates of the TBBPA gradually decreased, respectively, by 16.68, 16.57, 9.15, 4.99, 2.74, 0.73, and 0.39 % per hour. This phenomenon was caused by adsorption and competition between the intermediates and TBBPA. Watts and Dilly (1996) indicated that when the chemicals were adsorbed, the reaction activity between chemicals and HO• would decrease. In the initial stages of the reaction, ozone came in contact with TBBPA clearly, which has not been adsorbed by the soil, leading to a fast degradation reaction. Along with the reaction, the amount of TBBPA that had not been adsorbed decreased in the soil columnar reactor. At this point, it was necessary for the ozone to react with TBBPA, which was adsorbed on the soil surface or micropore, resulting in a constant decrease in the reaction rate. The results of this experiment are similar to those of the oxidation of ozone in the Philippines and benzene in the sand as reported by Choi et al. (2001). Additionally, the reactions of ozone and organic compounds contain a series of complex chemical steps, including the reactions between ozone and both the target compounds and the degradation products. In the reaction process between ozone and TBBPA, the amount of coproducts increased with the ongoing oxidation from ozone, inducing an acceleration of the reaction between ozone and TBBPA.

During the same period, the removal of TBBPA decreased with increasing soil depth. From the ozone breakthrough curve (Lu 2004), we can see that following the increase of soil depth and total amount of contaminants, the time that ozone required to penetrate the soil column reactor was prolonged.

The fact that ozone first dissolved in the moisture in the soil and reacted with TBBPA would prevent the transmission of ozone in the soil column reactor. In the process of transmission, the resistance of the ozone transmission associated with the TBBPA content, mass transfer, and chemical reactions would influence the penetrable ability of ozone (Sung and Huang 2002; Zhang et al. 2003). This is owing to the ozone transfer in the soil column, consisting of the advection diffusion in the pore gas and dissolution in the water which is bound to the surface of sand. Ozone reacted with the pollutants that had both dissolved into the soil and adsorbed onto the surface of the sand (Kim and Choi 2002). The existence of the chemical reactions can promote the conversion of ozone from gas to liquid (Sung and Huang 2002). The degree of this facilitation is determined by two parameters, the transient response factor and the Hatta number (Levenspiel 1999). These two parameters are related to the content of reactants and the degree of the promotion, from which we can acquire the breakthrough curve of ozone in the soil column. The curve indicates that the ozone transfers faster and consumes more with the increasing depth of polluted soil; therefore, it takes more time for ozone to penetrate the entire soil column reactor. We used the removal of TBBPA attained by consuming unit masses of ozone to represent the ozone utilization ratio. During the period of first 2 h, the ozone utilization ratios were 9.27, 9.22, 6.01, 4.81, and 1.6 ng TBBPA mg ozone⁻¹ with the soil depth ranging from 1–3, 4–6, 7–9, 10–12, and 13–15 cm of the column reactor. This suggested that in the wake of the soil depth raised, the amount of TBBPA that a unit mass of ozone was capable of removing reduced. This also indicated that the utilization of ozone, which dissolved in water and reacted with TBBPA, decreased. The primary cause of this

difference is that the mass transfer area became larger with the increase in soil depth (Pierpoint et al. 2003). More ozone dissolved in water led to less gaseous ozone, resulting in greater changes in the spatial distribution of gaseous ozone in the soil column. Therefore, along the direction of ventilation, the ozone that could dissolve in the water and react with pollutant decreased, causing a great change in the removal rate of TBBPA in the soil column.

Effect of the initial concentration of ozone

Because the ozone concentration could be an important parameter in controlling the degradation process, the effect of the initial concentration of ozone on the TBBPA degradation rate was investigated over the concentration range of 1–10 mg L⁻¹ (Fig. 2). The influence of the ozone concentration on the changes in the experimental progress was explored with the response time of the degradation of TBBPA, which was 2 h, and the soil depth, which was 15 cm. The percentages of TBBPA were 9.63, 12.52, 14.93, 61.48, and 67.11 % on the surface soil when ozone concentrations were 10, 7.5, 5, 3, and 1 mg L⁻¹, during 2 h. As shown in Fig. 2, the degradation effect of TBBPA gradually improved with an augment in ozone concentration. When the ozone concentration was 10 mg L⁻¹, the degradation rate was highest; TBBPA removal rate reached 90.27 % in the soil, with the greatest rate at surface soil. The degradation rate of TBBPA correspondingly declined with the concentration of ozone reduced. When the ozone concentration reduced to 1 mg L⁻¹, the TBBPA removal rate was only 32.89 % in the surface and was lower in the soil of greater depth.

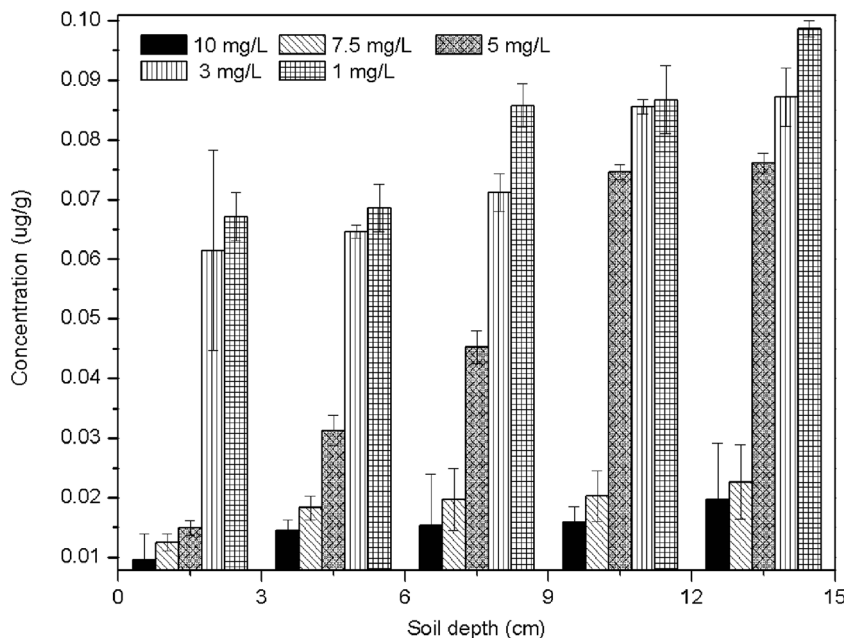
The time required by ozone to penetrate the entire soil column reactor was reduced with the improvement in ozone concentration for more ozone molecules that were able to dissolve in the moisture of the soil and react with the TBBPA in the process of transmission. Moreover, the presence of the chemical reactions was able to accelerate the conversion of ozone from gas to liquid. The degree of promotion was determined by the transient response factor and Hatta number (Levenspiel 1999). On account of that, a higher concentration of ozone led to an abundant degradation of TBBPA in a short time, as there were less TBBPA remaining after 2 h. But as the reaction consumed more ozone molecules, the ozone that the deeper soils were able to utilize was greatly declined. Therefore, the degradation rate of TBBPA in deep soil was lower than the surface soil. The majority of ozone molecules consumed by surface soil were utilized to react with TBBPA, which result in a low degradation rate in the deep soil.

It can thus be seen that TBBPA degraded most quickly with the highest ozone concentration (10 mg L⁻¹). A conclusion could be reached that these stringent conditions were necessary to provide enough ozone exposure to overcome the scavenging capacity of the soil and produce greater ozonation in TBBPA.

Effect of irradiation experiments

All of the soil samples were kept in the dark, and the blanks were analyzed to establish that only UV light irradiation, not elevated temperatures, affected the samples. The results from these analyses indicated fairly good reproducibility. The soil samples indicated direct results with manifest abilities for

Fig. 2 The concentrations of TBBPA at the following five different ozone conditions: 10, 7.5, 5, 3, and 1 mg L⁻¹. Soil samples were taken from the column at different depths. Each column was run for 2 h



removing TBBPA when exposed to UV reactor. A conclusion could be achieved that TBBPA degradation was largely caused by photolysis (photolytic degradation of organobromines is noted type of reaction in basic chemistry) (Pierpoint et al. 2003); however, the contribution of other degradation approaches cannot be ignored in complex soil-water mixtures (Philippopoulos and Nikolaki 2010).

As shown in Fig. 3, the photodegradation under the UV lamps occurred more rapidly than that under sunlight, which was a result of the continuous light intensity in the UV light reactor and was higher than the natural solar light (Fig. 4). Intensity of irradiation has been demonstrated to be an important parameter impacting the degradation of organic chemicals by photoactivity (Feo et al. 2014; Bezares-Cruz et al. 2004; Lee et al. 2004; Park et al. 2003). The quantitative data straightforwardly indicated that TBBPA reduced rapidly under UV lamp irradiation; in the first 2 h, 41.23 % removal efficiency was observed. After exposed to UV light for 256 h, 83.29 % of the TBBPAs were removed through photodegradation. However, outdoor solar exposure was discontinuous, which result in a decrease of TBBPA at a slower rate than that in the indoor experiment. After being exposed to sunlight for 16 h, approximately 44.28 % of the TBBPAs were removed. When soil samples were exposed to sunlight for 256 h, the removal efficiency of TBBPA was 67.88 %. Lee et al. (2004) reported that the photodegradation rates of BPA increased with the enhanced intensity of the UV lamps. It is comparable between indoor and outdoor exposures, and the degradation occurs independently under continuous or discontinuous exposure. As a result, the degradation of TBBPA will also occur in places where sunlight is occasional. According

to the previous report, the irradiation intensity of UV light depends on latitude and time of the year and differs by a magnitude of approximately 10 from summer to winter (Josefsson 1996). As a consequence, the degradation of TBBPA will probably change based on season and location.

The effect of temperature on TBBPA degradation

Figure 5 shows two dynamic histograms of TBBPA under different temperatures. At the summer ground temperature of 40 °C, the removal efficiency of TBBPA attained the maximum percentage of 38.05 % when the residence time reached 30 days. At the room temperature of 25 °C, the degradation rate of TBBPA was much slower than that at high temperature. The removal rate of TBBPA was extremely slow, but the amount of TBBPA continued to slowly decrease during the 30 days. However, at room temperature, the TBBPA remained at 81.28 % on the 30th day, 18.72 % of TBBPA being degraded.

Some researchers believe that the emission and distribution of BFRs in the environment are due to temperature-controlled processes, such as condensation/deposition of emissions at cold temperatures and volatilization at warm temperatures (Wania and Mackay 1993; Hoff et al. 1996; Melymuk 2012). In the recent past, Wu et al. (2014) demonstrated that the lowest and highest hexabromocyclododecane (HBCD) concentrations were in the winter and summer, respectively. These variations may be a combining result of several factors, for instance, temperature and wet deposition. Previous studies have shown that the emission rates of HBCDs from flame-retardant-treated textiles increased with temperature

Fig. 3 The concentrations of TBBPA under indoor UV lamp irradiation and outdoor solar light irradiation. Soil samples were taken at 2, 4, 8, 16, 32, 64, 128, and 256 h

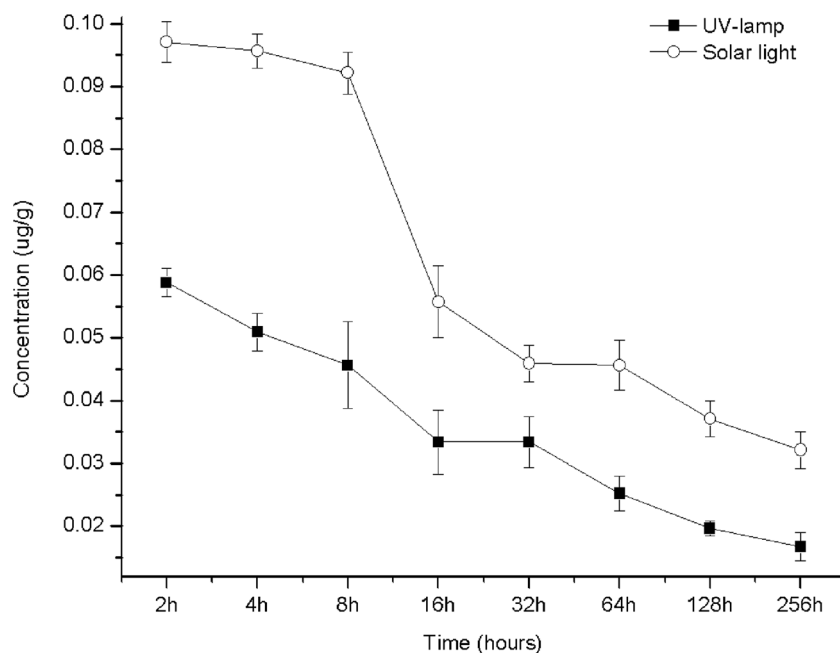
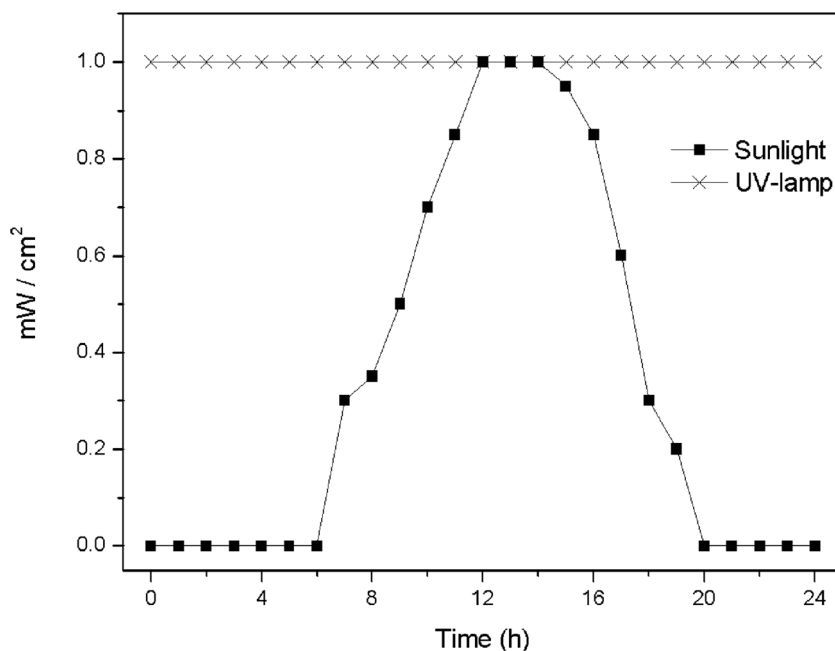


Fig. 4 UV irradiation indoors vs. outdoors



(Kajiwara and Takigami 2013). The result suggested that HBCD emissions from industrial materials and electrical and electronic appliances can be expected to accelerate with promoting temperature. Thus, it can be seen that the organic matter behavior is similar to our experimental results and also suggests that the increase of temperature would accelerate organic matters to degrade and migrate. At high temperature, the degradation of TBBPA becomes more active. It therefore seems reasonable to consider that high ground temperature in the summer contributes to the degradation and transformation of TBBPA. It is necessary to test this hypothesis with further analyses based on a larger set of TBBPA and samples.

The effect of soil pH changes on TBBPA degradation

The degradation of TBBPA was studied at pH values between 2.0 and 9.0, as shown in Fig. 6. When the soil pH value was 7.0, the degradation of TBBPA was slow, as shown in Fig. 5. Compared to the TBBPA in neutral soil, changing soil pH in the reaction system greatly improved the removal efficiency of TBBPA. As the Fig. 6 illustrates, when the soil pH value was approximately 9.0, the removal rate of TBBPA was the fastest. On the fifth day, the removal rate of TBBPA reached 28.12 %. The rest of TBBPA still decreased at a rapid rate, and reduced to 22.58 ng g⁻¹ until the 30th day, that is, the

Fig. 5 The concentrations of TBBPA for 30 days at the summer average high temperature of 40 °C and room temperature of 25 °C, sampling every 1, 2, 3, 4, 5, 12, 18, 24, and 30 days for a total of nine times. In addition, the concentrations of TBBPA for 30 days at the room temperature were the result of the control treatment of this study

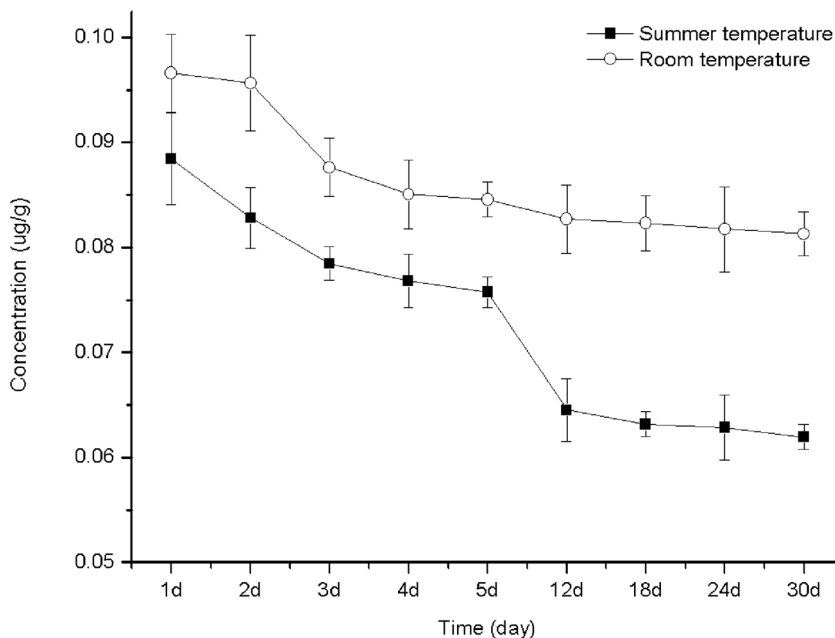
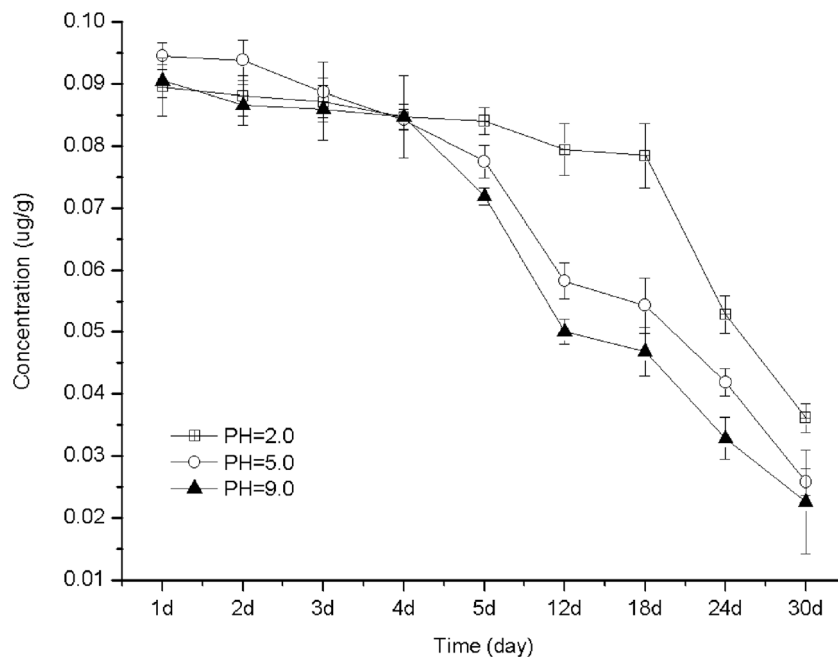


Fig. 6 The concentrations of TBBPA at soil pH values of 2.0, 5.0, and 9.0 over 30 days. Sampling every 1, 2, 3, 4, 5, 12, 18, 24, and 30 days, totaling nine times



degradation of 77.42 % of TBBPA. When the soil pH value was approximately 5.0, the removal rate of TBBPA was comparable to that of the slightly alkaline soil. The concentration of TBBPA reduced to 77.5 ng g⁻¹ on the 5th day and gradually decreased to 25.78 ng g⁻¹ in the 30th day. Removal rate of TBBPA in acid soil was at a relatively low rate compared to TBBPA in slightly alkaline and weak acid soil. The concentration of TBBPA was still 78.47 ng g⁻¹ on the 18th day and dropped to 36.11 ng g⁻¹ at the 30th day.

Contrasting the concentration of TBBPA in the four groups of the soil samples, it can be observed that the order of degradation intensity was pH=9.0 > pH=5.0 > pH=2.0 > pH=7.0, indicating that the degree of degradation of TBBPA was higher for samples with a pH change than those without pH change. This strongly suggests that the pH value is an important factor affecting the degradation of TBBPA. In weakly alkaline soil, the degradation behavior of TBBPA was much more obvious. Kang and Ge (2010) concluded that PAHs in the soil columns with different pH values had different vertical migration behaviors. Lowering PAHs had strong vertical migration capability in soil columns with higher pH levels, while higher-ring PAHs had strong vertical migration capability in soil columns with lower pH levels. These organic matters degradation behaviors also suggested that the change of pH value would affect the degradation and migration of organic matters.

Conclusions

The study outcomes demonstrate the following: (1) in the low atmospheric ozone concentration simulation experiments, the strong oxidizing ability of ozone was able to remove TBBPA

quickly. (2) The degradation reaction rate of TBBPA increased with an increase in ozone concentration but decreased with increasing soil depth. (3) The photodebromination rate increases with increase of the light intensity. Indoor and outdoor exposures are comparable, and the degradation occurs independently under continuous or discontinuous exposure. Therefore, the degradation of TBBPA will also occur in places where sunlight is occasional. (4) The condition of high ground temperature in the summer contributes to the degradation and transformation of TBBPA. (5) An alkaline soil environment was more conducive to the degradation and migration of TBBPA. In the natural environment, biodegradation by microorganisms or chemical reduction–oxidation can continuously degrade the products of TBBPA. These findings indicate that in photoreactions of TBBPA, the increase in atmospheric ozone concentration, environmental temperature, and soil pH are important processes during TBBPA degradation. These results could facilitate the amelioration of waste treatment designs and lead to better predictions of TBBPA fate in nature environment.

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References

Anonymous (1992) Biodegradation and bioaccumulation data of existing chemicals based on the CSCL. Chemicals Inspection & Testing Institute Toxicology and Information Center, Tokyo

- Arbeli Z, Ronen Z (2003) Enrichment of a microbial culture capable of reductive debromination of the flame retardant tetrabromobisphenol-A, and identification of the intermediate metabolites produced in the process. *Biodegradation* 14:385–395
- Berger U, Herzke D, Sandanger TM (2004) Two trace analytical methods for determination of hydroxylated PCBs and other halogenated phenolic compounds in eggs from Norwegian birds of prey. *Anal Chem* 76:441–452
- Bezares-Cruz J, Chad T J, Hua I (2004) Solar photodecomposition of decabromodiphenyl ether: products and quantum yield. *Environ Sci Technol* 38(15):4149–4156
- BSEF (2003) Major brominated flame retardants volume estimates. Available: http://www.bsef.com/docs/BFR_vols_2001.doc
- BSEF (2006) An introduction to bromine. Available: http://www.bsef.com/docs/BSEF_Bromine_intro.pdf
- Chen JW, Guo ZM (2012) The summer high temperature climate characteristics and abnormal flow analysis of Fugang County. *Guangdong Meteorol* 34:33–34
- Chen DH, Bi XH, Zhao JP, Chen LG, Tan JH, Mai BX, Sheng GY, Fu JM, Wong MH (2009) Pollution characterization and diurnal variation of PBDEs in the atmosphere of an E-waste dismantling region. *Environ Pollut* 157:1051–1057
- Choi HK, Kim YY, Lim H, Cho J, Kang JW, Kim KS (2001) Oxidation of polycyclic aromatic hydrocarbons by ozone in the presence of sand. *Water Sci Technol* 43:349–356
- Covaci A, Voorspoels S, Abdallah MAE, Geens T, Harrad S, Law RJ (2009) Analytical and environmental aspects of the flame retardant tetrabromobisphenol-A and its derivatives. *J Chromatogr A* 1216:346–363
- Darnerud PO (2003) Toxic effects of brominated flame retardants in man and in wildlife. *Environ Int* 29:841–853
- de Wit CA, Alaee M, Muir DCG (2006) Levels and trends of brominated flame retardants in the Arctic. *Chemosphere* 64:209–233
- Ding LJ, Wang CL, Ling LX (2011) Spatial-temporal variation characteristics of average temperature in Guangdong Chinese. *J Agrometeorol* 32:500–506
- Fackler P (1989) Determination of the biodegradability of tetrabromobisphenol A in soil under aerobic conditions. *Springborn Life Sciences, Inc, Wareham*
- Feo ML, Gonzalez O, Baron E, Casado M, Piña B, Esplugas S, Eljarrat E, Barceló D (2014) Advanced UV/H₂O₂ oxidation of deca-bromo diphenyl ether in sediments. *Sci Total Environ* 479–480:17–20
- George KW, Häggblom MM (2008) Microbial O-methylation of the flame retardant tetrabromobisphenol-A. *Environ Sci Technol* 42:5555–5561
- Hakk H, Letcher RJ (2003) Metabolism in the toxicokinetics and fate of brominated flame retardants—a review. *Environ Int* 29:801–828
- Hoff RM, Strachan WMJ, Sweet CW, Chan CH, Shackleton M, Bidleman TF, Brice KA, Burniston DA, Cussion S, Gatz DF, Harlin K, Schroeder WH (1996) Atmospheric deposition of toxic chemicals to the great lakes: a review of data through 1994. *Atmos Environ* 30:3505–3527
- Hornung A, Balabanovich AI, Donner S, Seifert H (2003) Detoxification of brominated pyrolysis oils. *J Anal Appl Pyrolysis* 70:723–733
- Huang YQ, Wong CKC, Zheng JS, Bouwman H, Barra R, Wahlstrom B, Neretin L, Wong MH (2012) Bisphenol A (BPA) in China: a review of sources, environmental levels, and potential human health impacts. *Environ Int* 42:91–99
- Huang DY, Zhao HQ, Liu CP, Sun CX (2014) Characteristics, sources, and transport of tetrabromobisphenol A and bisphenol A in soils from a typical e-waste recycling area in south China. *Environ Sci Pollut Res* 21:5818–5826
- Josefsson W (1996) Five years of solar UV-radiation monitoring in Sweden. *SMHI Reports Meteorology and Climatology No.71: 0347-2116*
- Kajiwara N, Takigami H (2013) Emission behavior of hexabromocyclododecanes and polybrominated diphenyl ethers from flame-retardant-treated textiles. *Environ Sci* 15:1957–1963
- Kang Y, Ge XL (2010) Simulation experiments on influences of pH level on the vertical migration of polycyclic aromatic hydrocarbons in soils. *Rock Miner Anal* 29:123–126
- Kim J, Choi H (2002) Modeling in situ ozonation for the remediation of nonvolatile PAH-contaminated unsaturated soil. *J Contam Hydrol* 55:261–285
- Lee JM, Kim MS, Kim BW (2004) Photodegradation of bisphenol-A with TiO₂ immobilized on the glass tubes including the UV light lamps. *Water Res* 38:3605–3613
- Levenspiel O (1999) Fluid-fluid reactions: kinetics in chemical reaction engineering, 3rd edn. John Wiley & Sons, New York, pp 523–539
- Liu J, Wang Y, Jiang B, Wang L, Chen J, Guo H, Ji R (2013) Degradation, metabolism, and bound-residue formation and release of tetrabromobisphenol A in soil during sequential anoxic-oxic incubation. *Environ Sci Technol* 47:8348–8354
- Lu J (2004) Studies on in-situ ozonation of PAH in simulated soil. *Wuhan University MdD, Wuhan*, p 16
- Luo CL, Liu CP, Wang Y, Liu X, Li FB, Zhang G, Li XD (2011) Heavy metal contamination in soils and vegetables near an e-waste processing site, south China. *J Hazard Mater* 186:481–490
- Melymuk L (2012) Semi-volatile organic contaminants in the urban atmosphere: spatial and seasonal distributions and implications for contaminant transport. *University of Toronto PhD, Toronto*, p 155
- Morris S, Allchin CR, Zegers BN, Hafka JJH, Boon JP, Belpaire C, Leonards PEG, van Leeuwen SPJ, 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
- Niu XJ, Liu C, Song XF (2015) Simulation research on the natural degradation process of PBDEs in soil polluted by e-waste under increased concentrations of atmospheric O₃. *Chemosphere* 118:373–382
- Park SE, Joo H, Kang JW (2003) Photodegradation of methyl tertiary butyl ether (MTBE) vapor with immobilized titanium dioxide. *Sol Energy Mater Sol Cell* 80:73–84
- Philippopoulos CJ, Nikolaki MD (2010) Photocatalytic processes on the oxidation of organic compounds in water. *Water Blandna Ramov New Trends Tech* 62:953–978
- Pierpoint AC, Hapeman CH, Torrents A (2003) Ozone treatment of soil contaminated with aniline trifluralin. *Chemosphere* 50:1025–1034
- Renner R (1997) European bans on surfactant trigger transatlantic debate. *Environ Sci Technol* 31A:316–320
- Ronen Z, Abeliovich A (2000) Anaerobic-aerobic process for microbial degradation of tetrabromobisphenol A. *Appl Environ Microb* 66:2372–2377
- Shih YH, Wang CK (2009) Photolytic degradation of polybromodiphenyl ethers under UV-lamp and solar irradiations. *J Hazard Mater* 165:34–38
- Sjödin A, Hagmar L, Klasson-Wehler E, Kronholm-Diab K, Bergman A (1999) Flame retardant exposure: polybrominated diphenyl ethers in blood from Swedish workers. *Environ Health Perspect* 107:643–648
- Sung M, Huang CP (2002) In situ removal of 2-chlorophenol from unsaturated soil by ozonation. *Environ Sci Technol* 36:2911–2918
- Thomsen C, Lundanes E, Becher G (2001) Brominated flame retardants in plasma samples from three different occupational groups in Norway. *J Environ Monit* 3:366–370
- Voordeckers JW, Fennell DE, Jones K, Häggblom MM (2002) Anaerobic biotransformation of tetrabromobisphenol A, tetrachlorobisphenol A, and bisphenol A in estuarine sediments. *Environ Sci Technol* 36:696–701
- Wang Y, Luo CL, Li J, Yin H, Li XD, Zhang G (2011) Characterization of PBDEs in soils and vegetations near an e-waste recycling site in south China. *Environ Pollut* 159:2443–2448

- Wania F, Mackay D (1993) Global fractionation and cold condensation of low volatility organochlorine compounds in polar regions. *Ambio* 22:10–18
- Watanabe I, Sakai SI (2003) Environmental release and behavior of brominated flame retardants. *Environ Int* 29:665–682
- Watts RJ, Dilly SE (1996) Evaluation of iron catalysts for the Fenton-like remediation of diesel-contaminated soil. *J Hazard Mater* 51:209–224
- Wong MH, Wu SC, Deng WJ, Yu XZ, Luo Q, Leung AOW, Wong CSC, Luksemburg WJ, Wong AS (2007) Export of toxic chemicals—a review of the case of uncontrolled electronic-waste recycling. *Environ Pollut* 149:131–140
- Wu MH, Zhu JY, Tang L, Liu N, Peng BQ, Sun R, Xu G (2014) Hexabromocyclododecanes in surface sediments from Shanghai, China: spatial distribution, seasonal variation and diastereoisomer-specific profiles. *Chemosphere* 111:304–311
- Yang H (2012) The ozone pollution of Pearl River Delta. *Yangcheng Evening News* 6A:3–28
- Zhang H, Song MH, Huang CP (2003) One dimensional model of in-situ ozonation for the remediation of phenanthrene-contaminated soil. *J Chem Eng* 17:466–470
- Zhang XL, Luo XJ, Chen SJ, Wu JP, Mai BX (2009) Spatial distribution and vertical profile of polybrominated diphenyl ethers, tetrabromobisphenol A, and decabromodiphenylethane in river sediment from an industrialized region of south China. *Environ Pollut* 157:1917–1923
- Zhi X, Wang J, Chai M, Chen ZP, Zhan ZS, Zheng WP, Wei XG (2011) Spatiotemporal variation of soil pH in Guangdong Province of China in past 30 years. *Chin J Appl Ecol* 22:425–430