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In Situ Microbial Degradation of PBDEs in Sediments from an E-Waste Site as Revealed by Positive Matrix Factorization and Compound-Specific Stable Carbon Isotope Analysis

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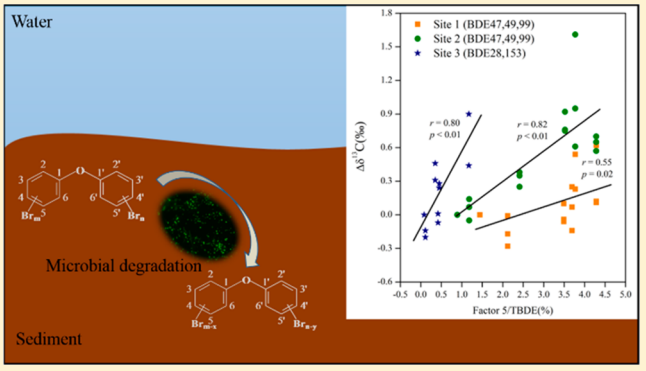
Supporting Information

ABSTRACT: In the present study, positive matrix factorization (PMF) and compound-specific isotope analysis were used to investigate the in situ biodegradation of polybrominated diphenyl ethers (PBDEs) in sediment cores collected from a pond at an e-waste recycling site in South China. The potential microorganisms relevant to the degradation of PBDEs were also assessed to aid in the understanding of in situ biodegradation. The PMF results suggested that reductive debromination took place in the sediments. The debromination signal (ratio of the concentration of factor 5 (PMF result) to the total PBDE content) was positively correlated with the relative abundance of *Dehalococcoidetes* at different core depths. The clear ^{13}C enrichment of five PBDE congeners (BDE 28, 47, 49, 99, and 153) with increasing core depth indicated that a measurable change in isotope fractionation might have occurred during PBDE biodegradation. The in situ biodegradation was further validated by the widespread detection of mono-BDE congeners (BDE 2, BDE 3) and diphenyl ether in the sediments. This study provides new evidence to enhance our understanding of the in situ biodegradation of PBDEs and suggests that the extensive removal of bromine from PBDEs was mediated by indigenous microorganisms at the e-waste site.



INTRODUCTION

In the past four decades, polybrominated diphenyl ethers (PBDEs) have been widely used as flame retardants in commercial electronic equipment and building materials, resulting in widespread contamination in the environment.[1] Owing to their highly lipophilic properties, PBDEs are found at extremely high levels in the sediment and biota of aquatic environments, especially at e-waste recycling sites.[2,3] As a result, PBDEs have become a global public health concern[4] and were recently included in the persistent organic pollutant (POP) list under the Stockholm convention.[5]

Despite their classification as persistent, PBDEs may be transformed by microorganisms, fishes, mammals, and ultraviolet light, as observed in a number of laboratory studies.[6−9] Anaerobic sediments are major sinks and environmental reservoirs for PBDEs; therefore, anoxic debromination by microorganisms is an important elimination route for PBDEs in the environment.[10] To date, studies have demonstrated the microbial reductive debromination of PBDEs under anaerobic conditions and even the complete debromination of PBDEs by *Dehalococcoides mccartyi* GY50.[6,10,11] However, in contrast to the abundant information on PBDE microbial degradation based on laboratory tests, the fate of PBDEs in natural sediments remains to be elucidated. Major challenges in assessing the in situ microbial degradation of PBDEs include the following: (1) a lack of information on PBDE sources in the natural environment, which makes it difficult to establish a chemical mass balance to trace the fate of PBDEs; (2) an exceptionally slow in situ degradation rate, which makes it hard to detect minor degradation signals; and (3) the inability of conventional methods based on concentration and composition information to distinguish the destructive and non-

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destructive removal of contaminants, which makes it difficult to identify debromination in the natural environment.

Positive matrix factorization (PMF) modeling has been shown to be able to determine source profiles and contributions. In particular, PMF is well suited to determine low-weight factors, ensuring that weak signals will be adequately represented.[12] Therefore, PMF should be useful to trace the degradation of PBDEs in sediments, even with minor degradation signals. Recently, PMF analysis has been successfully applied to identify and quantify the microbial reductive debromination of PBDEs by analyzing the presence of specific congeners in sediments from Arkansas water bodies,[13] the Great Lakes[14] and San Francisco Bay.[15] These studies show the potential for PBDE degradation in sediments, but no direct evidence of in situ biodegradation processes has yet been presented.

Currently, compound-specific isotope analysis (CSIA) has been shown to be a promising tool for improving the understanding of organic chemicals in in situ biodegradation processes. CSIA is based on the preferential transformation of lighter isotopes during degradation reactions; thus, heavier isotopes become enriched in the remaining substrate in the course of biodegradation.[16] Therefore, CSIA can provide evidence of the environmental attenuation of pollutants at different temporal and spatial scales when degradation products cannot be detected.[17] Thus far, CSIA has been widely employed to assess the in situ microbial degradation of chlorinated ethenes,[18] halogenated benzene,[19] and chlorpyrifos.[20] Laboratory studies have also shown the potential use of CSIA to trace the fate of PBDEs during photochemical transformation[21] and biotransformation in fish.[22] However, the application of CSIA in the microbial degradation of PBDEs has yet to be reported.

In this study, we combined PMF and CSIA to investigate the microbial degradation of PBDEs in sediments in a contaminated pond located in an e-waste region in South China. Previous investigations have suggested that the potential ability of sediments to remove PBDEs relies on the distribution and activity of indigenous bacteria, particularly dehalogenating bacteria, in the sediments.[11,23] Therefore, analytical procedures were developed as follows: (1) PMF modeling was applied to PBDE congener patterns to look for signs of debromination in sediments; (2) the potential microbes relevant to the degradation of PBDEs in sediments were assessed using high-throughput sequencing to aid in the understanding of in situ biodegradation; and (3) carbon isotope ratios of individual PBDE congeners were determined using CSIA for further proof of the microbiodegradation of PBDEs in field sediments.

MATERIALS AND METHODS

Sampling. A total of 40 composite sediment core samples were obtained, including 13, 14, and 13 samples for sites 1, 2, and 3, respectively, from a pond located in the town of Longtang, Qingyuan County, a typical region with the most intensive e-waste recycling activity in China, in 2016. The map of sampling sites detailed information regarding sampling region and sample collection are given in the Supporting Information (SI).

Sample Preparation. The sediments were freeze-dried, pulverized, and homogenized by sieving through an 80 mesh stainless steel sieve. The method used to extract and purify sediment samples for PBDE quantification and CSIA were similar to those described in previous studies,[3,24,25] with minor modifications, and detailed in the SI.

Instrumental Analysis. *1. Quantitative Analysis.* The PBDE congeners were quantified using a gas chromatograph/mass spectrometer (GC/MS) (Agilent 6890 N/5975B MSD; Agilent Technology, CA) in electron-capture negative chemical ionization (ENCI) mode. Detailed descriptions of the GC conditions and the ions monitored for PBDEs are given in the SI.

2. Qualitative Analysis of Mono-BDEs and Diphenyl Ether. Mono-BDEs and diphenyl ether (DE) were analyzed by an Agilent 7890A GC-5975C MS system with an electron impact (EI) ion source in full-scan mode. The qualitative identification of mono-BDEs and DE was achieved by comparing the mass spectra and retention times of the target compounds in samples with those of the standards. Detailed descriptions are given in the SI.

3. Stable Carbon Isotope Composition ($\delta^{13}C$) Analysis. The purity of the extracts used for CSIA was first checked using an Agilent 7890A GC-5975C MS system with an EI ion source in full-scan mode. In the present study, the $\delta^{13}C$ values of PBDE congeners were analyzed by a Trace GC Ultra-IsoLink Delta V Advantage isotope ratio mass spectrometer (Thermo-Fisher Scientific, Waltham, MA), and detailed descriptions can be seen in the SI.

Positive Matrix Factorization (PMF) Analysis. PMF is an advanced multivariate factor analysis tool, and EPA PMF version 5.0[26] was used for the calculations in our study. Further detailed descriptions of PMF analysis and the diagnostic tools used are provided in the SI.

Data Matrix. A total of 40 PBDE congeners were quantified in 40 sediment samples. Congeners with more than 50% nondetects and samples with nondetects in more than 13 congeners (35%) were eliminated from the data matrix. For the remaining congeners, the missing data were replaced by one-half of the method detection limit (MDL) for the congener. Site 1, 2, 3 are the three sampling sites located at the same closed pond, which was a closed pond near e-waste recycling workshops. Therefore, The PBDE data acquired from site 1, 2, and 3 were pooled for PMF analysis. A data matrix with 32 congeners and 31 samples was acquired (SI Table S2) and subjected to analysis in the EPA PMF 5.0 program. In all cases, the results are presented as an average (AV) with the standard deviation (SD) from the mean for 10 PMF runs with the same data matrix.

Identification of Potential PBDE Debrominating Microorganisms. 16S rRNA gene tag sequencing and data analysis based on Illumina high-throughput sequencing followed by taxonomic classification were used in the present study for microbial analysis. The details of these methods are described in the SI.

Data Deposition. Raw Illumina MiSeq sequencing reads were deposited into the European Nucleotide Archive (ENA) with accession no. PRJEB28854.

Quality Assurance and Quality Control (QA/QC). During sample analysis, a total of four laboratory method blanks, processed along with sediment samples, only detected traces of target compounds, including BDE 47 (0.43−0.72 ng/g, dw), BDE 99 (not detected (ND)−0.62 ng/g, dw), BDE 138 (ND−0.15 ng/g, dw), BDE 153 (ND−0.39 ng/g, dw), BDE 206 (1.75−3.39 ng/g, dw), BDE 207 (2.79−4.72 ng/g, dw), BDE 208 (2.44−3.49 ng/g, dw), BDE 209 (2.54−5.15 ng/g, dw). The percent recoveries of the surrogate standards

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ranged from 93% to 98% for BDE 77, BDE 181, BDE 205, and $^{13}C_{12}$−BDE 209. The analyzed concentrations have been treated by blank correction, but not by recovery correction. For the CSIA analysis, a PBDE standard mixture (BDE 28, 47, 77, 100, 99, 85, 154, 153) was tested twice a day in the process of analysis to ensure the stability of the instrument. The $\delta^{13}C$ values (AV ± SD) of PBDE standard mixture were −27.17 ± 0.12‰, −25.80 ± 0.13‰, −28.25 ± 0.12‰, −29.27 ± 0.14‰, −28.40 ± 0.09‰, −25.88 ± 0.13‰, −27.80 ± 0.12‰, and −29.23 ± 0.11‰ for BDE 28, 47, 77, 100, 99, 85, 154, and 153, respectively. A coinjected standard, 3,3′,4,4′-tetrabrominated diphenyl ether (BDE 77), whose $\delta^{13}C$ value was first determined offline with a Flash 2000 EADelta V Plus isotope ratio mass spectrometer (IRMS) (Thermo-Fisher Scientific), was spiked into the extract before CSIA analysis. The online-measured $\delta^{13}C$ value for BDE 77 added in samples (−28.37 ± 0.19‰) was close to the offline-measured value (−28.20‰), indicating the reliability of the instrument. Each extract was commonly analyzed in triplicate, and the data were only considered if the $\delta^{13}C$ values of the three injections did not vary by more than 0.5‰.

Statistical Analysis. Statistical analyses were performed using SPSS 19.0, and curve fitting was performed with Origin 8.0. The One Sample Kolmogorov−Smirnov test was employed to test the data normality prior to other statistical analysis. A one-way analysis of variance (ANOVA) with a post hoc Tukey's honest test was employed to test the differences in total organic carbon (TOC) content and $\delta^{13}C$ values of PBDE congeners among different sampling sites. The correlations among the debromination signal (factor 5/total PBDEs (TBDE)), relative abundance of *Dehalococcoidetes* and $\delta^{13}C$ were evaluated by Pearson's correlation analysis. The level of significance was set at $p = 0.05$ throughout the study.

RESULTS AND DISCUSSION

PBDE Concentrations. The total PBDE concentrations (sum of 40 congeners) in sediments ranged from 65 to 1.03 × 10^6 ng/g dry weight (dw), showing a clear decrease with an increase in the core depth (SI Figure S2). Generally, the PBDE concentrations from site 3 (median: 4.30 × 10^4 ng/g; range: 5 × 10^3−1.03 × 10^6 ng/g) were 1−2 orders of magnitude higher than those from site 1 (median: 530 ng/g; range: 65−9.80 × 10^4 ng/g) and site 2 (median: 510 ng/g; range: 122−1.25 × 10^5 ng/g). Due to their high hydrophobicities, PBDEs were expected to be associated mainly with organic carbon-rich particles. Therefore, the high PBDE concentrations at site 3 were reasonable because a higher TOC content was detected at site 3 (AV ± SD: 71.1 ± 65.5 mg/g) than at site 1 (AV ± SD: 29.5 ± 30.0 mg/g) and site 2 (AV ± SD: 19.9 ± 21.5 mg/g) (SI Table S1). BDE 209 was the most abundant congener in all samples (SI Table S3), consistent with the fact that deca mixtures are the predominant PBDE commercial mixtures used in electronic and electrical products.[27] As reported by La Guardia et al., low-molecular-weight congeners, for example, BDE 7, 15, 32, 35, and 37, were not previously detected in PBDE technical formulations, but they were detectable (for example, the mole fractions of BDE 7, 15, 32, 35, and 37 ranged from 0.02 to 0.24%, 0.04−1.15%, 0.08−0.52%, 0.02−1.11%, and 0.06−0.55%, respectively) in our sediment samples (SI Table S3). The relatively high abundance of low-bromine congeners in all the samples suggested that debromination likely occurred at the study sites.

PMF Analysis. The PBDE concentrations at a 30−44 cm depth at sites 1 and 2 were generally low; these low concentrations are of limited interest and were excluded from PMF analysis. The PBDE data selected in this study are presented in SI Table S2.

Five-factor EPA PMF solutions were appropriate for these studied data sets. Detailed information about the determination of the number of factors is given in the SI, including Tables S4, S5, and S6. Given the production and usage history of commercial PBDE mixtures[28,29] and e-waste generation records,[30] six PBDE technical mixtures (Great Lake Chemical (GLC) DE−71, Bromkal 70−5DE, GLC DE−79, Bromkal 79−8DE, Saytex 102E, and Bromkal 82−0DE) from La Guardia et al.[31] (SI Figure S3) were initially selected as possible sources to identify the extracted likely factors, and cos φ[13] was used to evaluate the similarity between the technical mixtures and the PMF-determined factors. The fingerprints of the PMF-determined factors and cos φ values are shown in Figure 1 and Table 1, respectively.

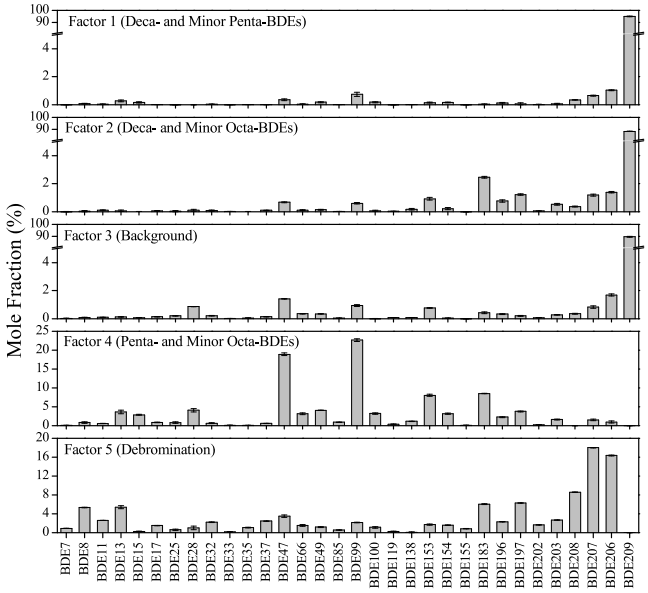

Figure 1. Five-factor positive matrix factorization fingerprints.

Table 1. Cos φ Values Characterizing the Similarity of Factors (PMF Analysis) to Technical PBDE Mixtures

	penta-BDE mixtures		octa-BDE mixtures		deca-BDE mixtures	
Cosφ	GLC DE−71	Bromkal 70−5DE	GLC DE−79	Bromkal 79−8DE	Saytex 102E	Bromkal 82−0DE
factor 1	0.01	0.01	0.02	0.88	1.00	1.00
factor 2	0.01	0.01	0.06	0.89	1.00	1.00
factor 3	0.02	0.02	0.03	0.88	1.00	1.00
factor 4	0.904	0.897	0.34	0.13	0.00	0.00
factor 5	0.15	0.15	0.43	0.34	0.02	0.06
factor 1[a]	0.86	0.82	0.13	0.12		
factor 2[a]	0.31	0.31	0.94	0.86		
factor 3[a]	0.75	0.77	0.31	0.26		

[a]Congeners 206, 207, 208, and 209 omitted.

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With regard to congener patterns, factors 1, 2, and 3 were dominated by BDE 209, with mole fractions of 95.0%, 88.3%, and 89.6%, respectively (Figure 1, SI Table S8), and the cos φ values were 1.00 for the deca mixtures (Saytex, 102E and Bromkal 82−0DE) (Table 1), which suggests a deca-BDE input. Less-brominated congeners that are abundant in commercial penta-BDE or octa-BDE formulations were also present in factors 1 through 3. As shown in Figure 1, factor 1 showed a high fraction of BDE 99, 47, and 100, and factor 2 showed a relatively high fraction of BDE 183, 153, 196, and 197, in addition to a high fraction of deca-BDE and nona-BDE congeners. When BDE 209 and nona-BDE congeners (BDE 206, 207, 209) were omitted in the calculations, the cos φ values were 0.86 (GLC DE−71) and 0.82 (Bromkal 70−5DE) for factor 1 and 0.94 (GLC DE−79) and 0.86 (Bromkal 79−8DE) for factor 2 (Table 1); therefore, additional minor penta- and octa-BDE input was recognized for factor 1 and factor 2, respectively. Similar to factor 1, the profile of factor 3 (without nona- and deca-BDEs) also resembled that of the penta-mixtures (cosφ = 0.75 for GLC DE−71 and 0.77 for Bromkal 70−5DE, Table 1), but factor 3 contained a higher mole ratio of BDE 47/BDE 99 (1.49) and a higher proportion of BDE 28 (0.87%) than would be expected from a penta-mixture (BDE 47/BDE 99:0.91 for GLC DE−71 and 1.11 for Bromkal 70−5DE; BDE 28:0.29% for GLC DE−71 and 0.12% for Bromkal 70−5DE). These elevated values indicated a weathered PBDE background in the sediment. This hypothesis rests on the fact that physical processes such as mixing, preferential transport, and partitioning may alter the original (source) congener patterns. Moreover, some evidence of debromination could not be ruled out, such as the debromination of PBDEs during the use and recycling of products that contain PBDEs. PMF analysis identified covarying congeners, which means congeners that are derived from the same location or process or even merely transported together. Therefore, weathering is a generic term that encompasses physical processes such as preferential transport and debromination. Thus, factor 3 may represent a weathered PBDE background associated with multiple routes, including debromination and physical processes.

Factor 4 strongly resembled the congener composition of penta-mixtures because it was dominated by BDE 47 (18.9%) and BDE 99 (22.7%) and the cos φ values of the penta-mixtures were 0.904 (GLC DE−71) and 0.897 (Bromkal 70−5DE) (Table 1; SI Table S8). Major congeners (BDE 183, 153, 197, and 196) in octa-mixtures were also present but did not dominate in factor 4, and the cos φ values were 0.34 (GLC DE−79) and 0.13 (Bromkal 79−8DE) for the octa-mixtures (Table 1). Therefore, factor 4 represented a dominant penta- but minor octa-BDE input, and the higher cos φ values for GLC DE−79 than Bromkal 79−8DE in sediment cores indicated that the GLC corporation is a source of the octa-BDEs.

Factor 5 was dominated by BDE 206, 207, and 208 with mole fractions of 16.4%, 18.0%, and 8.6%, respectively (SI Table S8). Gerecke et al.[32] reported that BDE 209 can be microbially degraded to nona-BDEs (BDE 208, 207, and 206) in anaerobic sewage sludge, suggesting that the high fraction of these nona-BDE congeners could be the consequence of microbial debromination in the sediment cores. More than 25% of factor 5 comprised congeners that are not present in the commercial mixtures (e.g., BDE 8, 11, 13, 32, 35, and 37) (Figure 1; SI Table S8)[31] and likely represent debromination products of higher-molecular-weight PBDE congeners. Previous studies reported that BDE 15 was a major debromination product of PBDE in photolysis.[33,34] However, factor 5 in this study contains quite a bit of BDE 17, a major microbial debromination products,[35,36] but almost no BDE15, suggesting that not photochemical reaction but microbial debromination is likely responsible for the debromination of PBDEs in sediments. Therefore, factor 5 was tentatively identified as a microbial debromination factor. This assumption was also supported by the low cos φ values (<0.5, Table 1) for the six commercial mixtures.

Factors 1, 2, and 3 mainly represented input from deca-BDE commercial mixtures; therefore, their contributions were combined (SI Figure S4a). As shown in SI Figure S4a, the total contributions of factors 1, 2, and 3 followed the patterns of total PBDE concentrations at all three sampling sites, decreasing with an increase in sediment depth, which is in accordance with the production and use history of deca-BDE commercial mixtures and the increasing rate of e-waste generation.[29,30] The contribution of factor 4 at the three sampling sites had a peak value in the 6 to 14 cm depth interval and then decreased with increasing sediment depth (SI Figure S4b), which might be the result of an accidental discharge of penta- and octa-BDE inputs. The contribution of factor 5 (debromination factor) generally showed an increasing trend from the bottom to the surface layer, with the exception of an obvious decreasing peak at depths of 12−20 cm at site 3 (SI Figure S4c). The proportion of factor 5 relative to the TBDE content was believed to represent the contribution of the debromination of PBDEs in the sediment cores. Therefore, the ratio of factor 5 to TBDE (factor 5/TBDE) at the three sampling sites was calculated, and the results followed the order site 1 (2.37 ± 0.09%) > site 2 (1.52 ± 0.12%) > site 3 (0.27 ± 0.07%) (SI Figure S4c). The debromination of PBDEs could happen in the sediment core at depth, in the surface sediment and then that sediment became buried over time, or in the water column (i.e., suspended sediment) that was then later buried in the sediment bed. In the present study, the increase in factor 5/TBDE vs depth, except for a decrease at a 24−41 cm depth at site 3, likely suggested in situ PBDE biodegradation in the sediment core at depth (Figure 3), and a similar increasing trend has been reported in previous studies.[13]

Microbial Community Composition and Debrominating Populations. High-throughput MiSeq sequencing of 16S rRNA gene amplicons was employed to profile the microbial community compositions of the sediment cores. Principal coordinate analysis (PCoA) showed that the microbial community composition shifted from the top layer to the bottom layer in all three sediments and that the microbial community composition at site 3 was obviously different from those at sites 1 and 2 (SI Figure S5). These community differences were largely due to the different physicochemical properties of the sediments. In the current study, comparable elemental contents (i.e., TOC, hydrogen, sulfur and nitrogen) were observed for sites 1 and 2 (SI Table S1), which were different from site 3; in particular, a higher TOC content was observed at site 3 than that at site 1 (p = 0.018) or site 2 (p = 0.004). The different elemental contents and ratios (SI Table S1) may represent different environmental matrices, resulting in distinct community compositions. In addition to the physicochemical properties of the sediment, toxic organic compounds can also drive changes in the distribution of

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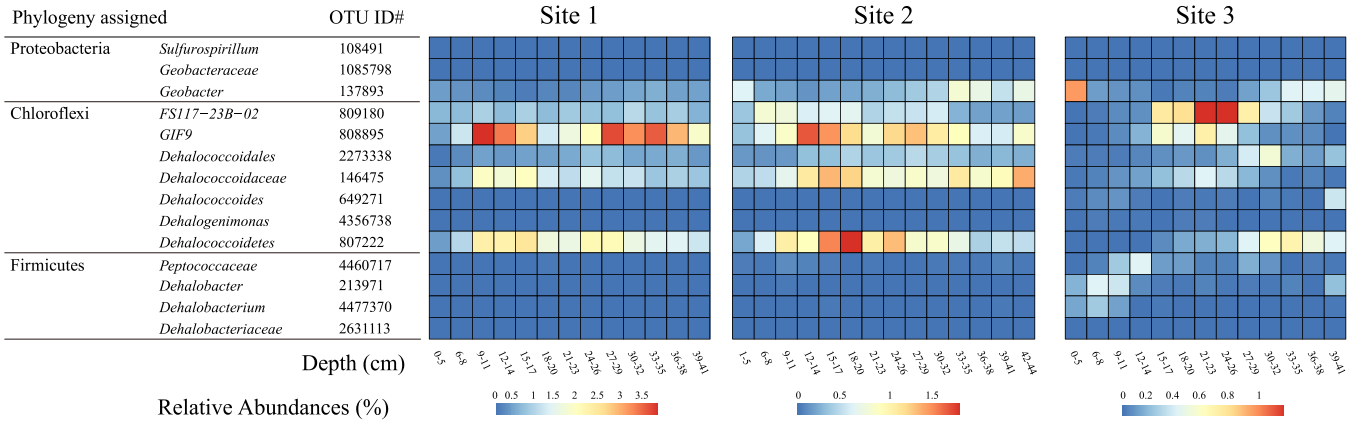

Figure 2. Relative abundance of putative dehalogenating bacteria in sediment cores. (FS117−23B−02 and GIF9 are the temporary name for the uncultured microorganism in the class of *Dehalococcoidetes* according to the GreenGene database.).

microbial populations.[37,38] Given the extraordinarily high content of PBDEs observed in the present study, it is reasonable to assume that the microbial community composition, particularly the putative PBDE dehalogenators, was associated with PBDE pollution. Therefore, the putative PBDE dehalogenators in the sediments were further examined to reveal potential in situ PBDE biodegradation.

According to previous studies,[13] putative dehalogenating bacteria of the *Proteobacteria*, *Chloroflexi*, and *Firmicutes* phyla were investigated for PBDE debromination. The experimental evidence showed that 14 populations had dehalogenation capacity and were present in the studied sediments (Figure 2). The elevated relative abundance of these dehalogenating bacteria indicated that the microbial degradation of PBDEs likely occurred in the studied sediments. Among these lineages, the isolates such as *Sulfurospirillum*, *Dehalococcoides*, and *Dehalobacter* confirmed the role in environmental debromination of PBDEs.[10] However, due to the limited information on organohalide-respiring bacteria (OHRB), those uncultured OHRB (e.g., in the class of *Dehalococcoidetes*) could also have a chance to contribute to the debromination in the sediment samples.[13,39] Moreover, *Dehalococcoidetes* within *Chloroflexi* was generally the dominant dehalogenating bacteria (Figure 2), accounting for 34.5−91.0% of the total putative dehalogenating bacteria in sediment samples. Therefore, all the following analyses mainly focused on *Dehalococcoidetes*. Similar to the trend of factor 5/TBDE, the relative abundance of *Dehalococcoidetes* in sediments generally followed the order site 1 > site 2 > site 3, with a range of 1.61% to 9.02% at site 1, 1.47% to 5.24% at site 2, and 0.20% to 2.55% at site 3.

Based on the PMF results, factor 5 represents the microbial debromination factor. A laboratory study reported that the growth of dehalogenators (*Dehalococcoides*) links tightly with PBDE debromination.[6] We expected that the contribution of factor 5 might be influenced by the relative abundance of *Dehalococcoidetes*. In fact, this expectation was confirmed by the positive correlation between factor 5/TBDE and the relative abundance of *Dehalococcoidetes*, although this correlation was not significant for sites 1 and 2 (Figure 3). It may be possible to gain a better correlation using the absolute abundance of Dehalococcoidetes. Therefore, to get a comprehensive information on debromination process in these sites, further quantitatively characterizing investigations are needed, along with other bioinformatics technology such as metagenome.

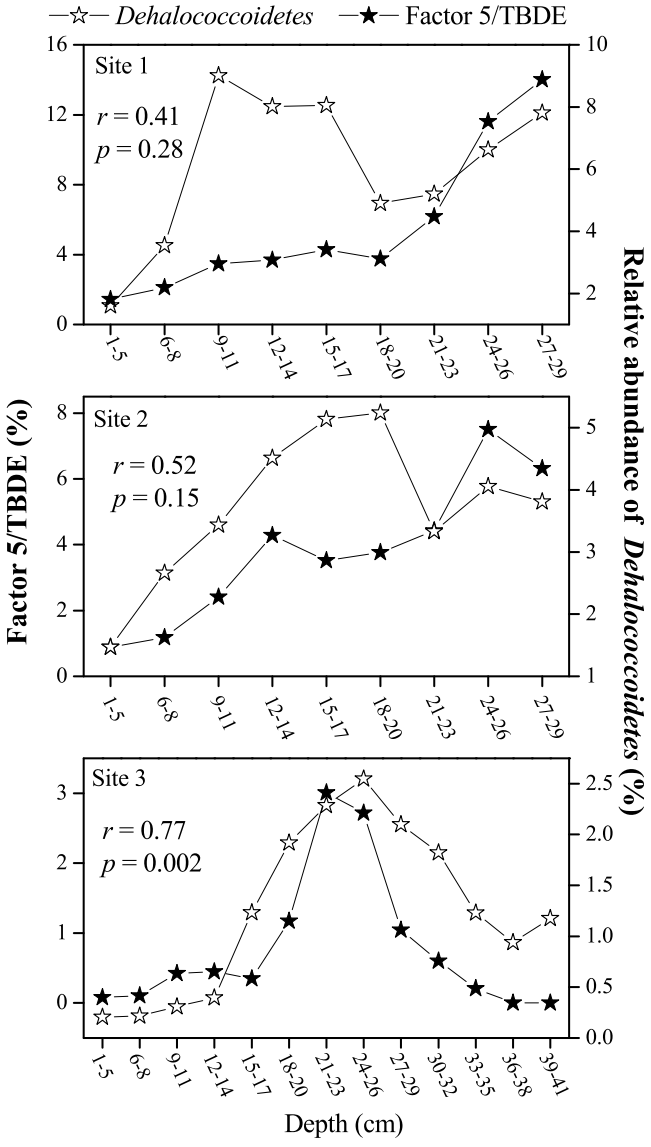

Figure 3. Ratio of debromination (EPA PMF factor 5) to total PBDE concentration (TBDE) at different depth intervals, including the relative abundance of all lineages of *Dehalococcoidetes*.

Compound-Specific Carbon Isotope Data. The PMF results and abundant dehalogenators provided clues about the

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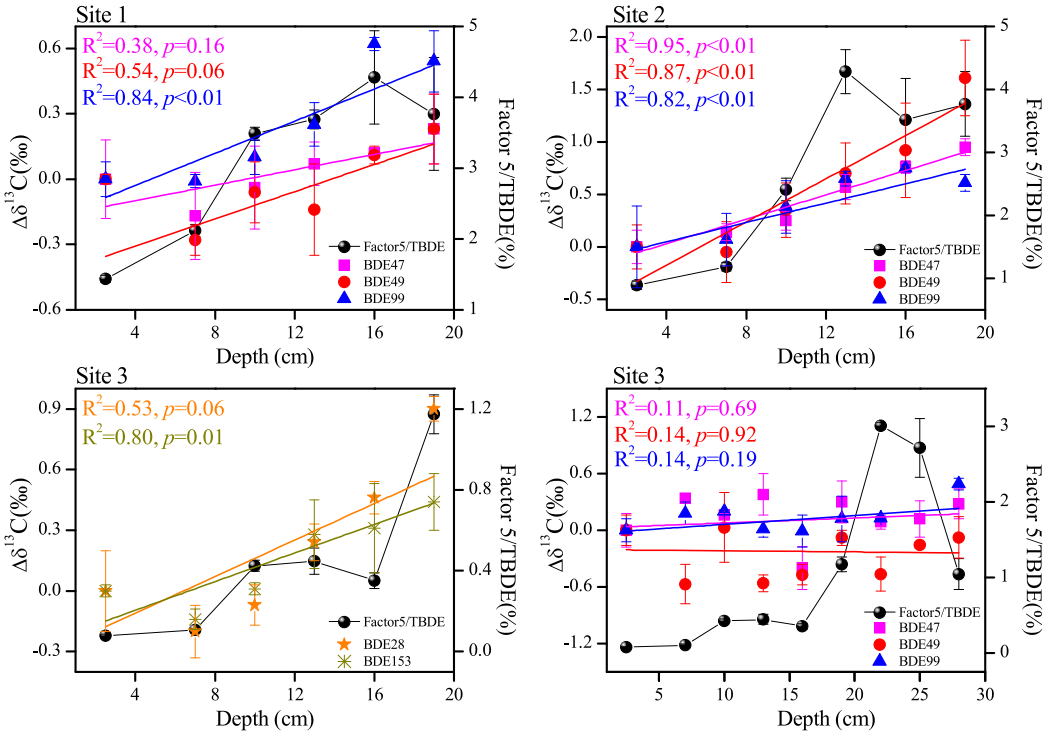

Figure 4. $\Delta\delta^{13}C$ values (‰) and factor 5/TBDE ratios (%) of PBDEs in sediments. $\Delta\delta^{13}C$ is the $\delta^{13}C$ value of PBDE congeners in each interval relative to that in the top interval (0–5 cm).

possible microbial degradation of PBDEs in sediments. To obtain further evidence, the $\delta^{13}C$ values of PBDEs in the sediment at different depth intervals were measured. Accurate $\delta^{13}C$ values could only be obtained for congeners with a well-resolved peak and a high concentration. In this study, the stable carbon isotope composition could only be determined for congeners BDE 47, 49, and 99 in the top layers (0–20 cm) of site 1 and site 2 and for BDE 28, 47, 49, 99, and 153 in the top layers (0–20 cm for BDE 28 and 153, and 0–29 cm for BDE 47, 49 and 99) of site 3, with the exception of BDE 99 in the 24–26 cm interval at site 3, which had interference from unresolved complex mixtures (UCM). The GC–MS full-scan chromatograms of these PBDE congeners in the sediment extracts are shown in SI Figure S6.

The $\delta^{13}C$ values of BDE 47, 49, and 99 in the sediments were in the range of −26.85 ∼ −26.45‰, −28.35 ∼ −27.84‰, and −29.18 ∼ −28.54‰, respectively, for site 1; −26.74 ∼ −25.79‰, −28.34 ∼ −26.67‰, and −28.77 ∼ −28.02‰, respectively, for site 2; and −26.61 ∼ −25.83‰, −27.31 ∼ −26.71‰, and −28.88 ∼ −28.38‰, respectively, for site 3 (SI Table S7). BDE 99 was more depleted in ^{13}C than BDE 47 and BDE 49 (BDE 47/49: Site 1: $p < 0.01/p < 0.01$; Site 2: $p < 0.01/p < 0.01$; Site 3: $p < 0.01/p < 0.01$), which is generally similar to the stable carbon isotope variations observed in PBDE commercial mixtures; that is, more negative $\delta^{13}C$ values are observed with an increasing degree of bromination.[40] However, in this study, the $\delta^{13}C$ values of BDE 28 (−27.22 ∼ −26.11‰) and BDE 153 (−28.56 ∼ −27.97‰) at site 3 were comparable to those of BDE 47/49 and BDE 99, respectively (BDE 28 & BDE 47/49: $p = 0.321$; BDE 153 and BDE 99: $p < 0.01$), which was different from the tendency observed in commercial mixtures (SI Table S7). These differences are likely due to the complex sources of PBDE congeners in natural sediment, as the isotope data for a PBDE congener can differ when the method or location of production of the congener is different.[40] For example, the $\delta^{13}C$ value of BDE 153 (−27.4 ± 0.63‰) originating from the octa-mixtures is higher than that of BDE 153 (−33.6 ± 0.004‰) from the penta-mixture and even higher than that of BDE 99 (−29.3 ± 0.20‰).[40] We hypothesize that in addition to different sources, the debromination of PBDEs can also be an important reason for the different trends of $\delta^{13}C$ values in this study. For example, BDE 28 can be the debromination product of higher-brominated congeners, such as BDE 47,[36] and this process will make BDE 28 more depleted in ^{13}C than the parent compounds (e.g., BDE 47); however, BDE 28 can also be degraded into lower-brominated congeners,[6] which make BDE 28 enriched in ^{13}C relative to BDE 47. Therefore, these processes are a reasonable explanation for why the $\delta^{13}C$ value of BDE 28 is comparable to that of BDE 47. In fact, the above hypothesis was further supported by the enrichment in the $\delta^{13}C$ values of BDE 28 and BDE 47 with increasing core depth (Figure 4) and the widespread detection of lower-brominated congeners (Figure 1 and SI Figure S7).

Relationship between the PMF and the Compound Specific Isotope Signatures. As suggested by the above analysis, anaerobic microbial debromination, which we speculate is associated with factor 5, may have occurred in the sediments. A comparison between the potential trends of PBDE $\delta^{13}C$ values and the debromination signal (factor 5/TBDE) at different sediment depths could provide insight into the in situ microbial degradation of PBDEs. As seen in Figure 4, there was a clear ^{13}C enrichment ($\Delta\delta^{13}C$: $\delta^{13}C_{\text{each interval}}$-$\delta^{13}C_{\text{top interval}}$) of BDE 47, 49, and 99 in sediments from site 1 and site 2 and BDE 28 and 153 in sediments from site 3 with increasing sediment depth. These increases were also in accordance with the increasing trends in factor 5/TBDE vs.

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depth, especially for BDE 99 (p = 0.042) at site 1; BDE 47 (p = 0.021), BDE 49 (p = 0.046) and BDE 99 (p = 0.002) at site 2; and BDE 28 (p = 0.025) at site 3. The ^{13}C enrichment and these similar trends suggest that these congeners underwent significant microbial degradation in the sediment cores over time, as degradation generally results in ^{13}C enrichment in the native congeners due to the kinetic isotopic effect.[22,41] Theoretically, isotope fractionation could be caused by both anaerobic and aerobic degradation, but the later seems less important than the former, because of the reduced anoxic conditions in the sediment cores[13,42] and the positive correlation between $\delta^{13}C$ change and debromination signal aroused by anaerobic dehalogenators.[23,43,44] Moreover, mono-BDE congeners (BDE 2, BDE 3) and DE, which are not present in the commercial mixtures, were widely detected in the sediment samples in the present study (SI Figure S7). This presence indicates that the PBDEs in the sediment cores likely underwent extensive bromine removal by dehalogenating microorganisms, generating mono-BDEs and DE in situ. These findings were also supported by the results of previous laboratory studies; that is, BDE 47→17→4 and BDE 99→47→18 were found to be dominant debromination pathways from a penta-BDE mixture in a sediment-free enrichment culture,[45] and the complete debromination of BDE 99 (BDE 99→47→28→15→3→DE) and BDE 47 (BDE 47→28→15→3→DE) were determined in a coculture consisting of *Dehalococcoides* and *Desulfovibrio* species.[6] Specifically, the production of mono-BDEs and DE could also contribute to a measurable effect on $\delta^{13}C$ values besides the debromination factor. On the other hand, the existence of these congeners (BDE 28, 47, 49, 99, 153) in debromination factor indicated that they are formed from debromination of higher brominated congeners (Figure 1, SI Table S8). Therefore, BDE 28, 47, 49, 99, and 153 could be intermediate congeners that were decomposed and formed during the PBDE biodegradation in studied sediments. These complicated metabolic processes and the lack of specific carbon isotope enrichment factors make it impossible to quantify the extent of isotope fractionation. Further studies are needed to characterize in situ PBDE microbiodegradation.

Unlike site 1 and site 2, there was no obvious trend in ^{13}C changes ($\Delta\delta^{13}C$) vs depth for BDE47, 49, and 99 at site 3, indicating that no significant isotope fractionation occurred (Figure 4). Given the extraordinarily high BDE 47, 49, and 99 levels observed in sediments from site 3 (BDE 47:642−5940 ng/g; BDE 49:141−1447 ng/g; BDE 99:636−5808 ng/g, dw), approximately 1 order of magnitude higher than those from site 1 (BDE 47:66−1179 ng/g; BDE 49:19−227 ng/g; BDE 99:104−1608 ng/g, dw) and site 2 (BDE 47:11−414 ng/g; BDE 49:3−110 ng/g; BDE 99:13−503 ng/g, dw) (SI Table S2), and the lower relative abundance of *Dehalococcoidetes* in site 3 (0.20−2.25%) than those in site 1 (1.61−9.02%) and site 2 (1.47−5.24%), the amount of BDE 47, 49, 99 degraded might be far less than those not degraded, and this speculation was further supported by the factor 5/TBDE, which revealed a lower degradation signal of PBDEs from site 3 (0.27 ± 0.07%) than those from site 1 (2.37 ± 0.09%) and site 2 (1.52 ± 0.12%) (SI Figure S4c). Therefore, this lack of obvious $\delta^{13}C$ changes in these congeners could be explained by the low PBDE degradation percentage, as the high abundance of unaltered native PBDE congeners would even out slight changes; similar findings were also determined in our previous study.[46] Moreover, the isotope fractionation caused by the removal of one bromine could be diluted by the other 11 carbons that are not involved in the reaction.[47]

In summary, we provided reliable evidence of in situ PBDE microbiodegradation using multiple-line-of-evidence-approaches including PMF, CSIA, and 16S rRNA sequencing. This study not only verified the results of PMF,[13,15] but also demonstrated the potentials of CSIA for in situ biodegradation assessment. What's more, given the worldwide distribution of PBDE manufacturing corporations and e-waste recycling sites,[48,49] more researches are needed for further characterizing the PBDE degradation in these hot spot sites.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b06110.

Additional details regarding sampling region, sample collection, sample preparation, instrumental analysis, PMF analysis, and microbial diversity, including Figures S1−S7 and Tables S1−S9 (PDF)

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