Major sources of MeO/OH-BDEs in the East China Sea elucidated from their records and phytoplankton biomarkers

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Abstract

Hydroxylated (OH-) and methoxylated (MeO-) polybrominated diphenyl ethers (PBDEs) have caused much concern because of their potential toxicity and worldwide distribution. These compounds are recently suggested to originate from the natural process in the ocean. However, their source remains highly controversial. In this study, we analyzed the contents of nine MeO-BDEs, ten OH-BDEs, and phytoplankton biomarkers (PBs) in two sediment cores collected from the East China Sea (ECS). The detection of 6-MeO-BDE-47, 20-MeO-BDE-68, and 6-OH-BDE-47 have been reported since the 1920s, prior to the production of PBDEs. Significant relations were found between MeO/OH-BDEs and indicators of marine organic matters. The similar down-core variations and significant correlations between MeO/OH-BDEs and PBs suggest the possibility that phytoplankton produced these natural compounds. Laboratory incubation further demonstrates that phytoplankton can produce MeO-BDEs. Comparisons between the content ratios of 6-MeO-BDE-47/20-MeO-BDE-68 and brassicasterol/dinosterol indicate that the signature of MeO-BDEs is controlled by the phytoplankton community structure.

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1. Introduction

Polynbrominated diphenyl ethers (PBDEs) have emerged as contaminants because of their ubiquitous environmental occurrences and potential adverse effects on organisms (Law et al., 2006). Their structural analogs, including methoxylated (MeO-) and hydroxylated (OH-) PBDEs, have also been widely detected in environmental substrates, such as algae (Asplund et al., 2001; Kuniyoshi et al., 1985; Malmbärg et al., 2005, 2008), fish (Valters et al., 2005; Zhang et al., 2010), marine animals (Fu et al., 1995; Kelly et al., 2008; Liu et al., 2012), sediments (Bradley et al., 2011; Zhang et al., 2012) and even humans (Hovander et al., 2002; Lacorte and Ikonomou, 2009; Stapleton et al., 2009; Wan et al., 2010a). Some species of MeO/OH-BDEs have shown equivalent toxic effects to PBDEs (Wiseman et al., 2011), so identifying their source has attracted increasing interest. These compounds were initially considered as metabolites or by-products of anthropogenic PBDEs because of the similarities in their structure (Haglund et al., 1997; Marsh et al., 2006). Some in vivo and in vitro studies have reported the biotransformation of OH-BDEs from various PBDEs (Erratico et al., 2010; Hakk et al., 2009; Malmberg et al., 2005; Qiu et al., 2007; Stapleton et al., 2009) despite the absence of OH-BDE formation in other PBDE exposure experiments (Benedict et al., 2007; Browne et al., 2009; Stapleton et al., 2006; Wan et al., 2009). However, concentrations of detected OH-BDEs were markedly lower than PBDEs, with a conversion ratio of ~3% (Erratico et al., 2010; Hamers et al., 2008; Malmberg et al., 2005; Stapleton et al., 2009). A recent study has reported that the time trends of PBDEs are different from those of OH-BDEs in blue mussels (Löfstrand et al., 2011). Hence, OH-BDEs are unlikely to originate from the anthropogenic PBDEs. Detectable contents of MeO-BDEs were not observed in controlled exposure studies (McKinney et al., 2006; Wan et al., 2010b, 2009; Zhang et al., 2010), and thus MeO-BDEs are expected to be natural compounds.

Recent studies have employed 14C isotope techniques (Guitart et al., 2011; Teuten et al., 2005) and demonstrated that 6-MeO-OH-BDEs are natural compounds.
BDE-47, 2′-MeO-BDE-68, 6-OH-BDE-47, and 2′-OH-BDE-68 in marine biological samples, with OH-/MeO- functional group substituted in the ortho position of the diphenyl ether backbone (ortho-substituted MeO/OH-BDEs), are from natural sources. Since the 1980s, these compounds have been widely detected as the dominant congeners of oxygenated PBDEs in sponges (Bowden et al., 2000; Carté and Faulkner, 1981; Fu et al., 1995; Handayani et al., 1997), algae (Asplund et al., 2001; Kuniyoshi et al., 1985), and marine animals at high trophic levels (Asplund et al., 2001; Verreault et al., 2005). On the basis of early marine pharmacological research (Faulkner et al., 1994), marine sponges are commonly considered as one of the main producers of these natural compounds. However, the widespread distribution of these natural compounds in the oceans, even in the Arctic regions, is difficult to elucidate considering their limited inhabiting regions (tropical oceans) (Kelly et al., 2008; Letcher et al., 2009; Verreault et al., 2005; Wan et al., 2009).

Guitart et al. (2011) speculated on the existence of unidentified marine producers with life cycles that occur in the surface of the ocean by comparing Δ14C values of MeO/OH-BDEs isolated from a whale (Teuten et al., 2005) and sponges (Guitart et al., 2011; Reddy et al., 2002) in different sea regions. In these samples, Δ14C values of these compounds presented a relatively wide range, from 17.2‰ to 119‰. They presumed that the Δ14C > 100‰ values of the bioaccumulated MeO-BDEs in a whale from the North Atlantic coast (Teuten et al., 2005) could correspond to marine planktonic organisms with higher turnover rates because of high enrichment in post-bomb 14C from surface waters, rather than bioaccumulated sponge-cyanobacteria metabolites. Löfstrand et al. (2011) also elucidated that filamentous macroalgae are potentially important producers of MeO/OH-BDEs on the basis of the seasonal variations in their concentrations in blue mussels from the Baltic Sea. These results indicate that the specific origins of these ortho-substituted MeO/OH-BDEs remain unclear.

This study was designed to verify the assumption of unidentified producers of MeO/OH-BDEs and to clarify their main sources in marine environments. MeO/OH-BDEs and biomarkers of brassicaterol, dinosterol, and alkenones were determined in two sedimentary cores collected from the East China Sea (ECS). Comparisons of these compounds and their derived indicators and laboratory incubations of microalgae were performed to verify whether MeO/OH-BDEs could be produced by phytoplankton. To our knowledge, this study is the first to utilize organic geochemical proxy to study the potential producers of naturally occurring MeO/OH-BDEs.

2. Material and methods

2.1. Sample collection

The ECS, one of the largest shelf seas in the world, is a river-dominated sea surrounded by the Kuroshio Current in the east, the Taiwan Strait in the south, Chinese mainland in the west, and the Yellow Sea in the north (Fig. 1). The ECS receives the discharge from the Yangtze River, and it's an important reservoir for sedimentary OM burial because of high river inputs and marine primary productivity. The sampling sites are located around the deposition center of the ECS, with stable sediment rates since the Holocene (DeMaster et al., 1985; Liu et al., 2007). Two sediment cores were collected in August 2009 during the summer cruise of CHOICE-C, using RV DongFangHong2 of the Ocean University of China (OUC). Fig. 1 shows the location of DH33 and KP04 in the offshore areas of the Zhejiang and Fujian coast, with relatively minimal human disturbance. Sediment core DH33 was collected in a hypoxic zone (Wang et al., 2012) (123°35.059’ E, 29°16.964’ N) close to the Yangtze River estuary, where the sediment is silt-dominated and influenced by the Taiwan
Warm Current (Xu et al., 2012). This area is characterized by intensive primary productivity (Liu et al., 2010). Core KP04 was sampled north of Taiwan Strait (121°00′54E, 26°04′28′′N), where the sediment is sand-dominated and influenced by both the Taiwan Warm Current and the China Coastal Current (Xu et al., 2012). Primary productivity in this area is lower compared with DH33 (Liu et al., 2010). Both cores were sectioned at 2 cm intervals, freeze-dried, homogenized, and stored at –20 °C until analysis.

2.2. Microalgae culture

Chaetoceros curvisetus (diatom), Prorocentrum donghaiense (dinoflagellate), and Emiliania huxleyi (coccolithophorid) were obtained from the Research Center for Micro Algae, OUC. The cultures used in this study are unicellular and axenic. Seawater that was used to prepare the medium was collected from the ECS and stored at 4 °C until analysis.

2.3. Sediment core dating

Sedimentation rates were determined from depth profiles of excess 210Pb (210Pbex) (Fig. 2). The total 210Pb and the fraction of the total 210Pb that is supported by its precursor, 226Ra, were measured to obtain 210Pbex. Due to the very short half-life of all intermediate nuclides between 226Ra and 210Pb, it is generally believed that supported 210Pb is in secular equilibrium with its precursors from 226Ra to 210Pb. We employed gamma spectrometry to determine simultaneously the activities of 210Pb and 214Pb on the basis of photon energies at 46.52 and 351.93 keV, respectively. We obtained the activity of excess 210Pb (210Pbex = 210Pb - 210Pb) by subtracting the activity of 214Pb from that of the measured (i.e., total) 210Pb. In theory, the activity of 210Pbex is the highest at the core top and decreases down-core because of radioactive decay. Therefore, the depth profile of 210Pbex can be described as

\[ C = C_0 \exp(-\lambda t) \]  

where \( C \) is 210Pbex at depth \( Z \), \( C_0 \) is 210Pbex at the core top (i.e., \( Z = 0 \)), \( \lambda \) is the decay constant of 210Pb (0.0331 yr⁻¹), and \( t \) is the post-depositional time. Given that \( t = \frac{Z}{S} \), where \( S \) indicates sedimentation rate, Eqn. (1) can be transformed to

\[ C = C_0 \exp(-\lambda Z / S) \]  

Thus, by plotting \( C \) versus \( Z \) on a semi-log plot, we expect to see straight lines, with slopes equal to \( -\lambda / S \), from which \( S \) can be determined.

More details on the gamma-spectrometry method, including the standard materials used to calibrate the detectors and QA/QC of the data, can be found elsewhere (Huh et al., 2011).

2.4. Analysis of MeO/OH-BDEs and lipid biomarkers

Sample extraction, cleanup, and instrumental conditions for MeO/OH-BDEs followed the methods established by Sun et al. (2012) with some modifications. The samples were extracted in an ultrasonic bath, cleaned by acid silica gel and a silica gel column, and then concentrated/solvent exchanged prior to GC/MS or LC/MS analysis. The procedures for analyzing lipid biomarkers of phytoplankton followed previous methods (Xing et al., 2011b). A detailed description of the methods is provided in the Supplementary Content.

2.5. Quality assurance and quality control

The mean recoveries (n = 3) for all the analytes in the sediments assessed by spiking each compound ranged from 71% to 108%. Recoveries of spikes ranged from 71.3% to 93.2% (13C-6-OH-BDE-47) and 73.5% to 81.6% (13C-6-MeO-BDE-47). The method detection limits (MDLs) for BDEs, MeO-BDEs, and OH-BDEs were lower than 0.34, 8.4, and 1.5 pg/g dw, respectively. All glassware were rinsed with dichloromethane and hexane and then baked at 400 °C for 6 h to avoid contamination. A method blank (anhydrous sodium sulfate) was coupled with every batch of 12 samples, and the target compounds were under MDLs in blanks.

3. Results and discussion

3.1. Sediment chronology

Fig. 2 shows the profiles of 210Pbex in the two studied cores, and the results indicated that the sedimentary environment in the core locations is stable. The sedimentation rates estimated from the slopes were 0.28, 0.52, and 0.15 cm/year for the core DH33, upper part (0 cm–14 cm) of KP04, and lower part (14 cm–24 cm) of KP04, respectively.

3.2. Occurrence of MeO/OH-BDEs

Of the 9 MeO-BDEs, 6-MeO-BDE-47 and 2′-MeO-BDE-68 were detected in most sections of the two sediment cores (Table SI-1). The predominance of the two compounds has often been observed in biotic media (Kelly et al., 2008; Wan et al., 2009), marine sediments (Zhang et al., 2012), and seawater (Vetter et al., 2009). The 6-MeO-BDE-47 and 2′-MeO-BDE-68 contents in core KP04 ranged from 18.7 pg/g dw to 29.0 pg/g dw and from 23.0 pg/g dw to 47.7 pg/g dw, respectively. Their corresponding values in core DH33 ranged from 24.2 pg/g dw to 91.2 pg/g dw and 19.8 pg/g dw to 35.9 pg/g dw. Their contents in the surface sediments (0 cm–2 cm) of cores KP04 and DH33 (29.0 pg/g dw and 91.2 pg/g dw for 6-MeO-BDE-47 and 47.7 pg/g dw and 33.1 pg/g dw for 2′-MeO-BDE-68) were higher than those in Liaodong Bay, China (15 ± 1.6 and 5.5 ± 1.9 pg/g dw for 6-MeO-BDE-47 and 2′-MeO-BDE-68, respectively) (Zhang et al., 2012) and White Lake in Michigan, USA (2.6 pg/...
g dw 6-MeO-BDE-47) (Bradley et al., 2011), and were comparable with those in Kootenay River in Genelle, Canada (43.7 ± 16 pg/g dw for 6-MeO-BDE-47) (Lacorte et al., 2010). Fig. 3 shows down-core variations in the contents of these compounds in both cores. No significant trend was observed from the 1920s to the 1970s, and an increasing trend emerged from the 1980s to the 2000s. MeO-BDEs were also detected in sediments in the early period (~1920s). Given that artificial PBDEs were produced after the 1960s (Ma et al., 2012), MeO-BDEs should be naturally occurring in the earlier period. The level of 2'-MeO-BDE-68 was higher than 6-MeO-BDE-

Fig. 3. Down-core variations in the contents of MeO/OH-BDEs and organic geochemical proxies in sedimentary core KP04 (A) and DH33 (B); MTOC = TOC × (1 – TMBR); ΣO-PBDEs mean total concentrations of MeO/OH-PBDEs, and ΣA + B + D indicates the total contents of brassicasterol, dinosterol, and long-chain alkenones.
47 in most of the core KP04 samples (Fig. 3, Table SI-1), whereas many previous studies have reported higher levels of 6-MeO-BDE-47 in biotic media and sediments (e.g. Kelly et al., 2008; Zhang et al., 2012).

Of the 10 OH-BDEs, only 6-OH-BDE-47 and 2′-OH-BDE-68 were detected in DH33 and KP04. In core DH33, the detection frequencies of 6-OH-BDE-47 and 2′-OH-BDE-68 were 100% and 46.2%, respectively, and their corresponding contents ranged from 13.5 pg/g dw to 83.9 pg/g dw and from 10.5 pg/g dw to 21.1 pg/g dw. In core KP04, the detection frequencies of 6-OH-BDE-47 and 2′-OH-BDE-68 were 100% and 12.5%, respectively, and their corresponding contents ranged from 12.9 pg/g dw to 23.4 pg/g dw and from 10.5 pg/g dw to 18.0 pg/g dw (Fig. 3, Table SI-1). 6-OH-BDE-47 and 2′-OH-BDE-68 were also shown as dominant species of OH-BDEs in marine organisms (Kelly et al., 2008; McKinney et al., 2006; Verreault et al., 2005; Wan et al., 2009; Zhang et al., 2010) and marine surface sediments (Zhang et al., 2012). The down-core variations of 6-OH-BDE-47 showed differences from those of 6-MeO-BDE-47 and 2′-MeO-BDE-68, fluctuating from the 1920s to the 1980s and increasing since the 1990s (Fig. 3). The detection of OH-BDEs in the 1920s also suggests that ortho-substituted OH-BDEs (6-OH-BDE-47) can originate from natural sources.

OM has been considered the potential factor controlling the accumulation of contaminants (such as PCBs and PAHs) in the sediments because of its high affinity to these compounds (Dunnivant et al., 2005; Zhang et al., 2009). Sedimentary total organic carbon (TOC) contents (%) were also analyzed to evaluate the effect of OM on the accumulation of 6-MeO-BDE-47, 2′-MeO-BDE-68, 6-OH-BDE-47, and 2′-OH-BDE-68. TOC is used as the indicator of primary productivity (Dunnivant et al., 2005; Zhang et al., 2009). Sedimentary total organic carbon (TOC) contents (%) were also analyzed to evaluate the effect of OM on the accumulation of 6-MeO-BDE-47, 2′-MeO-BDE-68, 6-OH-BDE-47, and 2′-OH-BDE-68. TOC in both cores showed a trend similar to the 6-MeO/OH-BDE-47 pair (Fig. 3). Significant relationships between the contents of 2′-MeO-BDE-68 and 6-MeO/OH-BDE-47 have also been found (Table 1, Figure SI-2). To our knowledge, this study is the first to report these relationships. The resemblance suggests that these ortho-substituted MeO/OH-BDEs may be from the same natural sources.

### 3.3. Linkage between different PBDE analogs

Previous studies have indicated significant relations between the OH-/MeO-BDE pairs in organisms (Wan et al., 2009) and sediments (Zhang et al., 2012), and even in in vitro and in vivo exposures (Wan et al., 2010b). In these two cores, 6-OH-BDE-47 and 6-MeO-BDE-47 presented a similar increasing trend from bottom to top (Fig. 3). Correlation analysis showed that these two compounds had a significant positive correlation in both cores ($r = 0.668, p < 0.05$ in KP04; $r = 0.639, p < 0.05$ in DH33). Similarities in down-core variations and significant correlations of the 6-OH-BDE-47/6-MeO-BDE-47 pairs can be attributed to their same origin or interconversion (Wan et al., 2010b, 2009). With the use of incubated slurry spiked with individual 6-MeO-BDE-47, 6-OH-BDE-47, and BDE-47, Zhang et al. (2012) confirmed that the MeO/OH-BDEs could be converted from their corresponding OH- or MeO-congeners via bacterial methylation and demethylation, rather than biotransformation of PBDEs. The natural relationship between these MeO/OH-BDEs has also been found in red algae (Malmvärn et al., 2005, 2008). We measured the contents of anthropogenic BDE-47 in the top and bottom samples in both cores. BDE-47 was undetected in the bottom samples, consistent with the fact that PBDEs were not produced or used in the early 20th century (Ma et al., 2012). Lower contents of BDE-47 were observed in the top samples (4.3 pg/g dw and 1.1 pg/g dw in cores KP04 and DH33, respectively), accounting for approximately 1.2% - 14.8% and 1.3% - 18.4% of the contents of 6-MeO-BDE-47 and 6-OH-BDE-47, respectively. Given these low conversion rates of PBDEs to OH-BDEs (Erratico et al., 2010; Hamers et al., 2008; Malmberg et al., 2005; Stapleton et al., 2009), PBDEs at lower levels or under-detection limits, but with higher levels of MeO/OH-BDEs in cores, indicate that the majority of MeO/OH-BDEs in marine environments did not originate from the biotransformation of PBDEs (Wiseman et al., 2011).

The down-core variations of the contents of 2′-MeO-BDE-68 in both cores showed a trend similar to the 6-MeO/OH-BDE-47 pair (Fig. 3). Significant relationships between the contents of 2′-MeO-BDE-68 and 6-MeO/OH-BDE-47 have also been found (Table 1, Figure SI-2). To our knowledge, this study is the first to report these relationships. The resemblance suggests that these ortho-substituted MeO/OH-BDEs may be from the same natural sources.

### 3.4. Linkage between MeO/OH-BDEs and marine producers

In marine environments, the major phytoplankton membrane lipids, namely, brassicasterol (B), dinosterol (D), and long-chain alkenones (A), are produced by diatoms, dinoflagellates, and coccolithophorids, respectively. These compounds are useful biomarkers to reflect the corresponding phytoplankton biomass in the euphotic layer (Schubert et al., 1998; Xing et al., 2011c; Zhao et al., 2006). The total contents of these lipids ($\Sigma A + B + D$) have also been proposed as a reliable indicator of MOM to distinguish them from total sedimentary OM (Ikehara et al., 2000; Xing et al., 2011b). Diatoms, dinoflagellates, and coccolithophorids dominate the phytoplankton, constituting the main component of primary productivity in the ECS (Guo et al., 2011; Yang et al., 2004). In this study, $\Sigma A + B + D$ was used as the indicator of primary productivity to study the importance of phytoplankton in producing ortho-substituted MeO/OH-BDEs. The down-core variations of $\Sigma A + B + D$ in both cores slightly fluctuated before the 1970s and then increased rapidly, similar to those of the ortho-substituted MeO/OH-BDEs (Fig. 3). Correlation analysis shows significant relationships between MeO/OH-BDEs and $\Sigma A + B + D$ (Table 1). In core DH33, the Pearson correlation ($r$) of 6-MeO-BDE-47 and $\Sigma A + B + D$

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**Table 1** Pearson correlations ($r, p < 0.05$) between the contents of MeO/OH-BDEs, $\Sigma A + B + D$, and MTOC in sedimentary core DH33 and KP04.

<table>
<thead>
<tr>
<th>Compounds and proxies</th>
<th>6-OH-BDE-47</th>
<th>6-MeO-BDE-47</th>
<th>2′-MeO-BDE-68</th>
<th>$\Sigma A + B + D$</th>
<th>MTOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>DH33</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6-OH-BDE-47</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6-MeO-BDE-47</td>
<td>0.639</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2′-MeO-BDE-68</td>
<td>0.741</td>
<td>0.948</td>
<td>1.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Sigma A + B + D$</td>
<td>0.658</td>
<td>0.930</td>
<td>0.659</td>
<td>0.903</td>
<td>1.000</td>
</tr>
<tr>
<td>MTOC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KP04</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6-OH-BDE-47</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6-MeO-BDE-47</td>
<td>0.668</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2′-MeO-BDE-68</td>
<td>0.607</td>
<td>0.974</td>
<td>1.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Sigma A + B + D$</td>
<td>0.744</td>
<td>0.678</td>
<td>0.704</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>MTOC</td>
<td>0.795</td>
<td>0.677</td>
<td>0.647</td>
<td>0.904</td>
<td>1.000</td>
</tr>
</tbody>
</table>

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*A stands for C37 alkenone, B stands for brassicasterol, D stands for dinosterol. MTOC = TOC / (1 - TMBR); "" stands for no significant correlation.
is larger than 0.9 (p < 0.05). The resemblance suggests that marine phytoplankton may be the key producers of MeO/OH-BDEs in the ECS (Malmvärn, 2007). These results also support the contention that unidentified marine producers inhabit the surface water of the ocean and produce these natural compounds (Guitart et al., 2011). Several studies have suggested that economic necessities in China enhance the anthropogenic nutrient inputs to the ECS and then increasing primary production (Li et al., 2007; Zhang et al., 2007). Given the lower transformation rates from PBDEs to OH-BDEs (Erratico et al., 2010; Hamers et al., 2008; Malmberg et al., 2005; Stapleton et al., 2009) and the natural characteristic of MeO/OH-BDEs (Guitart et al., 2011; Teuten et al., 2005), we speculate that the anthropogenic nutrient inputs may enhance their production. Hence, the rapid increase in MeO/OH-BDEs and biomarkers in recent years (Fig. 3) may be attributed to the high primary production, resulting from coastal eutrophication (Li and Dag, 2004; Paerl, 2006). The rapidly increasing trend implies that the potential risk caused by these natural compounds may have increased in recent years despite their relatively lower levels in the ECS (Figs. 3 and Table SI-1).

Recent studies have proposed new indices based on biomarker ratios to identify and evaluate the contributions of TOM/MOM in sedimentary OM (Xing et al., 2011b). One index is the terrestrial and marine biomarker ratio (TMBR) (Xing et al., 2011b), defined as the relative abundance of \( \Sigma C_{27} + C_{29} + C_{31} \) n-alkanes, which are the most abundant n-alkanes produced by high plants (Xing et al., 2011a, 2011b; Zhao et al., 2000) to the sum of \( \Sigma C_{27} + C_{29} + C_{31} \) n-alkanes and \( \Sigma A + B + D \). We define a new indicator of MTOC to represent MOM, which is calculated as

\[
\text{MTOC} = \text{TOC} \times (1 - \text{TMBR})
\]

MTOC can be also used to indicate MOM mainly derived from phytoplankton. Fig. 3 shows the down-core variations of MTOC exhibiting a similar vertical pattern to that of MeO/OH-BDEs. Correlation analysis shows significant linear relations between the contents of MeO/OH-BDEs and MTOC (Table 1). The results again indicate that marine phytoplankton, which mainly inhabits surface waters, can produce these natural compounds (Guitart et al., 2011).

Considering the effectiveness of stable carbon isotopic analysis for source identification (Hedges and Oades, 1997), \( ^{13}C \) values of brassicasterol, dinosterol, alkenone, 6-OH-BDE-47 (methylated derivative), 6-MeO-BDE-47, and 2′-MeO-BDE-68 were measured by a gas-stable isotope mass spectrometer. The \( ^{13}C \) values of brassicasterol, dinosterol, and alkenone were \(-24.9_{\text{nuc}}^{\text{mm}}\), \(-24.5_{\text{nuc}}^{\text{m}}\), and \(-22.0_{\text{nuc}}^{\text{m}}\), respectively, but no \( ^{13}C \) data of MeO/OH-BDEs were obtained because of their lower contents. However, the \( ^{13}C \) values of these biomarkers, which display the characteristics of MOM (Hedges and Oades, 1997), were close to those of 6-MeO-BDE-47 and 2′-MeO-BDE-68 (\(-22.2_{\text{nuc}}^{\text{mm}}\) and \(-24.2_{\text{nuc}}^{\text{m}}\)) isolated from the blubber of a True’s beaked whale (Teuten et al., 2005), presumably suggesting their same origin of phytoplankton.

### 3.5. Linkage between signature of PBDE analogs and phytoplankton community

Comparing the contents of different MeO-BDE analogs in both cores showed that 6-MeO-BDE-47 contents were higher than 2′-MeO-BDE-68 in DH33, whereas contrasting result was found in KPO4 (Fig. 3, Table SI-1). Contrary patterns for brassicasterol and dinosterol were also observed in these two cores (Figures SI-3); with more dinosterol in DH33 as opposed to more brassicasterol in KPO4, reflecting the dominance of diatoms in the Fujian coastal area (Guo et al., 2011). The synchronized inversion between MeO-BDE congeners and sterols implies that the signature of MeO-BDEs is controlled by the phytoplankton community structure given that phytoplankton may be an important producer of MeO/OH-BDEs.

Previous studies have reported that biomarker ratios of phytoplankton are reliable indicators for reconstructing changes to the phytoplankton community structure because of their similar diagenetic properties and relatively well preservation in sediments (Hinrichs et al., 1999; Schubert et al., 1998; Xing et al., 2011c). In this study, we selected the content ratios between brassicasterol and dinosterol (B/D ratios) as the indicator of the phytoplankton community structure in the studied area. The ratios of 6-MeO-BDE-47/2′-MeO-BDE-68 (MeO47/MeO68) were used as the signature of MeO-BDEs, and the contradiction between these two ratios were performed to study the influence of community structure on MeO-BDE species. Fig. 4 shows that MeO47/MeO68 ratios are higher (from 0.6 to 2.8) when B/D ratios were < 1.1, but are relatively stable and lower (from 0.6 to 0.8) when B/D ratios were > 1.1. Comparing these two ratios in the same cores presents a similar down-core trend when B/D ratios were < 1.1, whereas no significant trend was observed when B/D ratios were > 1.1 (Figure SI-4). These results indicate that the signature of MeO-BDE congeners may be controlled by the phytoplankton community structure.

We attribute the production of MeO-BDEs to diatoms and dinoflagellates because of the lower biomass of coccolithophorids, as reflected by the low concentration of long chain alkenone (Figure SI-3) (Schubert et al., 1998). A binary model was utilized to estimate their contributions to these two MeO-BDE congeners. The equations are expressed as follows:

\[
C_{2-\text{MeO-BDE-68}} = f_{b1}C_b + f_{d1}C_d
\]

\[
C_{6-\text{MeO-BDE-47}} = f_{b2}C_b + f_{d2}C_d
\]

where \( C_{2-\text{MeO-BDE-68}} \), \( C_{6-\text{MeO-BDE-47}} \), \( C_b \), and \( C_d \) represent the TOC normalized contents of 2′-MeO-BDE-68, 6-MeO-BDE-47, brassicasterol and dinosterol, respectively, \( f_{b1} \) and \( f_{d1} \) represent the conversion coefficients of diatoms and dinoflagellates, respectively, on 2′-MeO-BDE-68. \( f_{b2} \) and \( f_{d2} \) represent the conversion coefficients of diatoms and dinoflagellates, respectively, on 6-MeO-BDE-47. The contents are normalized to TOC to eliminate the granularity and other effects. The values of \( f_{b1}, f_{d1}, f_{b2} \), and \( f_{d2} \) calculated from the experimental data were 0.004, 0.104, \(-0.057\), and 0.288, respectively. The higher values of \( f_{d1} \) and \( f_{d2} \) indicate that dinoflagellates are likely more prone to produce MeO-BDEs than diatoms.

![Fig. 4. Plot of content ratios of 6-MeO-BDE-47/2′-MeO-BDE-68 versus B/D.](image-url)
Three microalgae, Chaetoceros curvisetus (diatoms), Procerotremum donghaiae (dinoflagellate), and Emiliania huxleyi (coccolithophorid), were incubated to verify further whether these microalgae could produce ortho-substituted MeO/OM-BDEs. Ortho-BDEs were not detected, their origins from phytoplankton could not be excluded because of their formation from corresponding MeO-BDEs in marine environments. The remarkable difference in MeO-BDE concentrations in different algae (Table 2) also indicates that the composition of MeO-BDEs can be affected by the phytoplankton community structure.

### 4. Conclusions

In the sedimentary cores from the ECS, 6-MeO-BDE-47, 2′-MeO-BDE-68, and 6-OM-BDE-47 are the dominant congeners. Their distribution supports the speculation that phytoplankton may be an important source of ortho-substituted MeO-BDEs. Although OH-BDEs were not detected, their origins from phytoplankton could not be excluded because of their formation from corresponding MeO-BDEs in marine environments. The remarkable difference in MeO-BDE concentrations in different algae (Table 2) also indicates that the composition of MeO-BDEs can be affected by the phytoplankton community structure.

### Acknowledgments

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### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2014.04.037.

### References


Carté, B., Faulkner, D.J., 1981. Polybrominated diphenyl ethers from Emiliania huxleyi (coccolithophorid), were incubated to verify further whether these microalgae could produce ortho-substituted MeO/OM-BDEs. Ortho-BDEs were not detected, their origins from phytoplankton could not be excluded because of their formation from corresponding MeO-BDEs in marine environments. The remarkable difference in Table 2 also indicates that the composition of MeO-BDEs can be affected by the phytoplankton community structure.

### 4. Conclusions

In the sedimentary cores from the ECS, 6-MeO-BDE-47, 2′-MeO-BDE-68, and 6-OM-BDE-47 are the dominant congeners. Their detection has been reported since the 1920s, prior to the production of PBDEs. Similar down-core variations and significant correlations were found between MeO/BDEs and PBs as well as their derived MOM indicators. MeO-BDEs are also detected in the incubated microalgae. These results suggest that MeO/BDEs in the ECS are mainly natural compounds potentially produced by the phytoplankton. Furthermore, the composition of MeO-BDEs suggests that it is controlled by the phytoplankton community structure.

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