



# Global occurrence of polybrominated diphenyl ethers and their hydroxylated and methoxylated structural analogues in an important animal feed (fishmeal)<sup>☆</sup>

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## ARTICLE INFO

### Article history:

Received 30 May 2017

Received in revised form

30 October 2017

Accepted 16 November 2017

### Keywords:

Polybrominated diphenyl ethers

Hydroxylated polybrominated diphenyl ethers

Methoxylated polybrominated diphenyl ethers

Fishmeal

## ABSTRACT

Polybrominated diphenyl ethers (PBDEs) and their hydroxylated (OH) and methoxylated (MeO) structural analogues have been found widely distributed in aquatic ecosystems, and may exhibit potential adverse effects to humans due to their bioaccumulative behavior through food chain. Fishmeal is an important animal feed applied around the world and is generally of marine origin. However, the levels and sources of PBDEs in fishmeal have not been thoroughly evaluated and their structural analogues have not been reported to date. The present study collected ninety-two fishmeal samples from world main fishmeal producing area to determine 27 PBDEs, 10 MeO-PBDEs and 11 OH-PBDEs. The concentrations of  $\Sigma_{27}$ PBDEs,  $\Sigma_{10}$ MeO-PBDEs and  $\Sigma_{11}$ OH-PBDEs were in the ranges of 0.1–1498 (mean: 75.8), 1.14–881 (37.4) and 1.00–47.5 (8.17) ng/g lipid, respectively. PBDEs were found primarily correlated with the historically commercial production, meaning higher production of certain commercial product in a country, higher corresponding PBDE congeners in local fishmeal. A market shift from penta- and octa-formulations toward deca-formulation was observed. BDE209 was identified as a major congener in fishmeal. Both the MeO-PBDEs and the OH-PBDEs were influenced by fishmeal producing areas ( $p < 0.001$ ). High MeO-PBDEs were identified in the Southeast Asian fishmeal, which might be due to the suitable environmental conditions for the generation of bromoperoxidase-contained algae in local area. The ratio of two major MeO-PBDE congeners, 6-MeO-BDE47/2'-MeO-BDE68, were generally  $>1$  in the northern hemisphere and  $<1$  in the southern hemisphere in the present study, which was consistent with the results obtained from previous published papers. Both MeO-PBDEs and OH-PBDEs were in accordance with the specialties of naturally produced halogenated compounds.

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## 1. Introduction

Polybrominated diphenyl ethers (PBDEs) are among the most pervasive flame retardants. They are added to furniture, textiles, and building materials to improve product fire resistance. Due to the potential of bioaccumulation, long range transportation, and certain toxicities (Covaci et al., 2011), the penta-/octa-BDE mixtures were regulated in Europe in 2004 (EU Directive, 2003) and United States in 2005 (UNEP, 2007), and were officially listed in the Stockholm Convention in 2009 (Stockholm Convention Decision, 2009a; Stockholm Convention Decision, 2009b). Deca-

BDE, the largest volumes of commercial PBDEs ever produced and used, is voluntarily withdrawn in Europe (Earnshaw et al., 2015) and United States from the end of 2013 (EPA, 2009), but is allowed in the rest of the world until it is officially listed in the Stockholm Convention in 2017 (UNEP, 2017). After the restriction of penta- and octa- PBDEs, the demand for deca-PBDE increased significantly. Currently, the environmental loading of PBDEs is mainly due to direct manufacturing emissions and secondary release from using and disposal of product stock containing PBDEs (Wiseman et al., 2011). Though the levels were reported to descend after 2009 in marine sediment (Lee and Kim, 2015), PBDEs have shown a still high existence in fish/seafood due to their bioaccumulation from the ongoing sources (Cruz et al., 2015).

The structural analogues of PBDEs, such as the hydroxylated and methoxylated (OH- and MeO-) PBDEs, have been revealed as

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ubiquitous compounds in environmental matrices (Kim et al., 2014; Ueno et al., 2008), and terrestrial and aquatic ecosystems (Covaci et al., 2008; Kelly et al., 2008; Mizukawa et al., 2013) in the past two decades. OH- and MeO-PBDEs are not anthropogenic products. It was reported that OH- and MeO-PBDEs may be primarily produced by marine sponges (Vetter et al., 2002), red algae and cyanobacteria (Malmvärn et al., 2005). Also, potential inter-conversion might occur among PBDEs and their structural analogues (Wan et al., 2010b). Previous studies suggested that OH-PBDEs were potentially more toxic than the parent PBDEs (Athanasidou et al., 2008) and thus aroused environmental and health concerns. OH-PBDEs are structurally similar to thyroxine (T4) and could compete with T4 for binding to transthyretin and thus cause possible endocrine disruption effects (Kojima et al., 2009; Mizukawa et al., 2016). Even more concerning was that OH- and MeO-PBDEs are able to accumulate in high trophic predators (Barón et al., 2013; Kelly et al., 2008; Montie et al., 2010; Pena-Abaurrea et al., 2009) and bio-magnify through marine food chains (Weijs et al., 2009). Moreover, humans are not immune from exposure to these pollutants. Haraguchi et al. reported that the level of 6-OH-BDE47 was approximately 20-fold higher than BDE 47 in the serum of Japanese women (Haraguchi et al., 2016). Athanasidou et al. (2008) determined that people preferring fish had higher OH-PBDEs levels in their serum. Wan et al. (2010a) also attributed the relatively high OH-PBDEs in South Korean women's serum to the consumption of seafood. The profiles of OH-PBDEs and MeO-PBDEs in human serum were consistent with those in edible seaweed and fish (Haraguchi et al., 2016), which also implied that seafood might be the major source of OH-PBDEs and MeO-PBDEs in humans.

With a spate of researches, it was still difficult to conclude which were the essential elements manipulating levels and distribution patterns of MeO- and OH-PBDEs. One of the reasons was lack of convincing samples with generality and ubiquity on a large scale. The concentrations of compounds could be orders of magnitude different in even one species when considering different tissues. For example, MeO-PBDEs were detected almost 2000 times higher in shark liver than in serum (200 vs. 0.13 ng/g ww) (Haraguchi et al., 2009; Nomiya et al., 2011b) from the Japanese Ishimaki coast. Therefore, an easily collected, homogeneous, worldwide distributed sample is needed to evaluate the occurrence of PBDEs and their structural analogues from marine environment. Fishmeal is an excellent protein additive that is one of the most important animal feeds. Fishmeal is generally of marine origin, and it is widely used in the global animal farming industry, especially for pet, fish, poultry and pig feed. Generally, it is a uniform mixture of fish and is able to avoid bias of single sample. Therefore, fishmeal might be used as a good indicator of PBDEs and their structural analogues in marine environment.

Though MeO- and OH-PBDEs were reported ubiquitously in aquatic systems, to the best of our knowledge, there is no study investigating the levels and distribution patterns of them in fishmeal to date. According to the formula of the animal feed, fishmeal could account for 10%–40% in weight. Notably, fishmeal might become a main source of PBDEs and their structural analogues for these domestic animals. These contaminants might further transfer to humans through the feed-to-fork pathway. In the present study, we collected 92 fishmeal samples worldwide to investigate PBDEs and their analogues. The levels, profiles, and geographic distribution of these contaminants in fishmeal samples were identified. Moreover, the essential elements manipulating levels and the distribution patterns of these congeners were also discussed according to the geographical distribution of the fishmeal samples.

## 2. Materials and methods

### 2.1. Sample collection

Ninety-two fishmeal samples were collected during the year 2012 and 2013 in the present study. The fishmeal samples covered the most important fishmeal producing areas, and they were grouped into five subgroups according to their origin, as follows: United States (U.S.,  $n = 9$ ), China ( $n = 28$ , including 17 from north China and 11 from south China), South America ( $n = 45$ ; 8 from Chile, 35 from Peru and 2 from Ecuador), Europe ( $n = 5$ ; 4 from Russia and 1 from Denmark), and Southeast Asia ( $n = 5$ ; 2 from Vietnam, 2 from Thailand and 1 from Malaysia). Fishmeal is used as an important raw material for the production of animal feed. In this study, all the fishmeals were sampled from the Chinese feed factories' warehouses directly. According to the information of the labels attached on fishmeal bags, we could identify these fishmeals were worldwide collected, such like China, U.S., South America, Europe and Southeast Asia. Related information was collected in situ. All of the samples were wrapped with aluminum foil and sealed in plastic zip bags until they arrived in the laboratory. Next, the samples were kept under  $-18\text{ }^{\circ}\text{C}$  until analysis. The manufacturing techniques, fish types of raw materials and other information of the fishmeal were recorded in Table S1.

### 2.2. Reagents and materials

PBDE commercial standards that include twenty-seven congeners (BDE 3, 7, 15, 17, 28, 47, 49, 66, 71, 77, 85, 99, 100, 119, 126, 138, 153, 154, 156, 183, 184, 191, 196, 197, 206, 207 and 209) were purchased from the Wellington Laboratories (Guelph, Canada). The list both covers the most common anthropogenic PBDEs and low/high brominated congeners. Ten MeO-PBDE standards (6-MeO-BDE47, 2'-MeO-BDE68, 6-MeO-BDE85, 4-MeO-BDE42, 4'-MeO-BDE49, 3-MeO-BDE47, 5-MeO-BDE47, 5'-MeO-BDE99, 6'-MeO-BDE99 and 2'-MeO-BDE28) and eleven OH-PBDE (3-OH-BDE28, 2-OH-BDE28, 4-OH-BDE42, 3-OH-BDE47, 4-OH-BDE49, 5-OH-BDE47, 6-OH-BDE47, 2-OH-BDE68, 6-OH-BDE85, 5-OH-BDE99 and 6-OH-BDE99) were purchased from AccuStandard (New Haven, CT, USA). MBDE-MXG ( $^{13}\text{C}_{12}$  BDE 3, 15, 28, 47, 99, 100, 126, 153, 154, 183, 197, 207, 209) and MBDE-ISS-G ( $^{13}\text{C}_{12}$  BDE 79, 138, 206) that were purchased from Wellington Laboratories were used as clean-up standards and recovery standards for PBDEs and MeO-PBDEs, respectively.  $^{13}\text{C}_{12}$ -6-OH-BDE47 that was purchased from Wellington Laboratories was used as a clean-up surrogate standard for OH-PBDE. Pesticide-grade dichloromethane (DCM), n-hexane, methyl *tert-butyl* ether (MTBE), 2-propanol and HPLC-grade acetonitrile were purchased from J.T. Baker (Phillipsburg, USA), and the nonane was from Sigma-Aldrich (St. Louis, USA). Silica gel (0.063–0.100 mm) was purchased from Merck (Darmstadt, Germany). Anhydrous sodium sulfate (baked at  $660\text{ }^{\circ}\text{C}$  for 6 h), concentrated sulfuric acid and sodium hydroxide were of reagent grade (purity > 99.8%) and were purchased from Beijing Chemistry Company (Beijing, China).

### 2.3. Analytical method and quantification

The fishmeal samples were lyophilized to a moisture content of 12%. Before extraction, the samples were spiked with two surrogate standards (1 ng MBDE-MXG for PBDEs and MeO-PBDEs; 10 ng  $^{13}\text{C}_{12}$ -6-OH-BDE47 for OH-PBDEs). Next, the weighed 1.0 g samples were extracted in an ultrasonic bath for 20 min with 10 mL hexane: MtBE (1:1) and 2 mL 2-propanol twice. After 10 min of centrifuging at a speed of 3500 rpm, the supernatant was transferred to a conical flask. The combined extracts were evaporated by rotary evaporator (Heidolph, Germany) to constant weight to record the fat contents.

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