Journal of Hazardous Materials xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Bioaccumulation of persistent organic pollutants in stranded cetaceans from Taiwan coastal waters

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HIGHLIGHTS

- PBDEs were first measured in stranded dolphin in Taiwan.
- PBDE levels and congener profile correlated to dolphin gender, tissue type and body length.
- Predominant compound BDE-154 and BDE47 suggested the metabolic capability of cetacean for PBDEs.

ARTICLE INFO

Article history:
Received 2 September 2013
Received in revised form
24 November 2013
Accepted 29 December 2013
Available online xxx

Keywords:
Dolphins
PBDEs
Bioaccumulation
Tissue type
Blubber

ABSTRACT

This study focuses on analyzing PBDEs in the liver, muscle, and blubber tissues of stranded dolphins (*Stenella attenuate*) on the Taiwan coast to determine and compare the PBDE levels and distributions among tissue types. Total concentrations of 19 PBDEs (ΣPBDE) in male dolphins (9.97 to 436 ng/g fat) were significantly higher than in female animals (2.73 to 89.5 ng/g fat), implying gender variation in bioaccumulation and the possibility of generation transfer from mother to fetus during pregnancy. The levels of contamination varied among tissue type; contamination was higher in blubber than that in muscle or liver, suggesting a possible transformation and redistribution of these compounds in body burden. Aside from gender and tissue type, ΣPBDE concentrations also significantly correlated with body length, an indicator of dolphin age. PCA analysis results showed no significant difference in PBDE congener pattern distributions in blubber tissues, indicating that blubber may be the final storage of contaminants in cetaceans, and that bioaccumulation of PBDEs may be dependent on chemical properties. BDE-154 and BDE-47 were the predominant PBDE congeners in stranded dolphins, and their correlation with body length suggests the significant metabolic depletion of BDE-154 in this species and possible exposure to both penta-BDE and octa-BDE mixtures.

1. Introduction

Cetaceans are the top predators in marine ecosystems, and are prone to accumulating high concentrations of persistent organic pollutants (POPs) [1–3], especially in contaminated coastal waters [4]. Thus, POP levels and distribution in cetaceans are important indicators of the contamination status and its environmental impact in coastal waters. Furthermore, prior investigation indicated that even relatively low concentrations of POPs can cause negative effects on dolphins, including immune system impairment [5], anemia, and problems with thyroid hormone homeostasis [6]. However, little is known about the impact of these POPs in terms of bioaccumulation, and whether they cause of cetacean stranding.

Polybrominated dipheyl ethers (PBDEs), recognized as emerging contaminants, are a group of POPs used as flame-retardants in textiles, paints, furniture, electronic circuit boards, and plastics which have been heavily developed and produced in Taiwan for the last few decades. Several investigations in Taiwan coast sediments [7,8] and estuarine fishes [9] have found detectable PBDE levels. Although PBDEs are listed in Stockholm Convention and use of PBDEs has already been terminated in many countries, large amounts of PBDEs have already been released into the global environment. As a result of their environmental persistence and high production volume, PBDEs have become ubiquitous global contaminants [1,10–13].

Recent attention has been focused on the potential bioaccumulation of PBDEs in marine ecosystems, especially the highly

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http://dx.doi.org/10.1016/j.jhazmat.2013.12.057

brominated PBDEs (high molecular weight) and the persistent substituted chemicals. While direct exposure to commercial BDE mixtures is assumed to be the main source of PBDE uptake/accumulation in biota, it is plausible that debromination of parent congeners in various tissue of marine organisms may contribute to the loading of persistent BDEs in marine food webs [14–16]. Many studies have reported on the occurrence and distribution of PBDEs in marine ecosystems and concluded that the geographical and temporal variations of PBDEs in marine mammals are affected by many factors, including exposure to contaminant source, species, gender, and age, but little information is available on the variation of fate and distribution of these persistent compounds in different tissues of top predators. Isobe et al. [17] reported that PBDE concentrations in striped dolphins collected from 1978 to 2003 in Japan showed no significant differences between blubber, liver and muscle. In contrast, other studies demonstrated varying PBDE concentrations (lipid based) among the different tissues in the same individual [18,19]. Thus, tissue-specific distribution of PBDEs in cetaceans remains an unresolved issue.

Monitoring the PBDE levels in tissues of dolphins is necessary to understand the exposure and the risks posed by toxic contaminants. As PBDE values have not been investigated for marine mammals from the Taiwan coast, 19 PBDE congeners were investigated in greater detail in the mass-stranded species (*Stenella attenuate*), a common species in Taiwan waters. Blubber, muscle and liver tissues of stranded dolphins were analyzed in this study. The primary objectives of this study were to report the levels of PBDEs in dolphin blubber, muscle and liver, to assess factors affecting these concentrations, to compare PBDE levels to concentrations previously reported in the other areas, and to evaluate the PBDE congener distributions in different tissue types to gain insight into metabolic and accumulation pathways for PBDEs in these stranded dolphins.

2. Materials and methods

2.1. Sample collection and preparation

Eight pantropical spotted dolphin (*S. attenuate*) were collected on the northern Taiwan coast from stranding incidents ($n = 8$) occurring in September, 2007. Samples were collected from dolphins stranded in good condition. All 8 stranded dolphins were dead when they were discovered. Within 12 h post-mortem, whole animal samples were placed on ice and transported to the laboratory where standard length, weight and sex were recorded. After biometric measurements, the animals were dissected; the bubbler and spinalis (muscle) samples were taken from the left side in front of the dorsal fin. All the samples were stored in baked glass jars and frozen at −20 °C until analysis.

2.2. Extraction and chemical analysis

Freeze-dried tissue samples were extracted with dichloromethane at 100 °C and 2000 psi in a pressurized fluid extractor (ASE-300, Dionex, USA). The programmed extraction heating and static times were both 5 min and three extraction cycles were used for each sample. Lipids and other matrix interferences were removed from each extract by acetonitrile. Prior to lipid removal, a subsample of each extract was used for gravimetric lipid content determination [20]. The resulting organic phase was reduced to approximately 5 mL using a rotary evaporator (Buchi R-3000), and passed through a glass column packed with 8 g of 2.5% (w/v) deactivated florisil and baked anhydrous sodium sulfate. The organic portion was eluted twice with 35 mL of petroleum ether. The first 35 mL of eluent was discarded, while the second 35 mL of eluent was collected and concentrated to approximately 5 mL by rotary evaporation. The volume of extract was further reduced to less than 1 mL under a gentle stream of nitrogen (99.99%; purified by passage through an activated carbon column).

The sample analysis was performed using a Varian CP-3800 gas chromatograph coupled with a Model 320 mass spectrometer using negative chemical ionization (NCI) in the selected ion monitoring (SIM) mode. A VF-5MS (10 m, id = 0.53 mm, 0.25 μm film thickness) rapid capillary column was used for the determination of PBDE congeners. The initial column oven temperature (80 °C; held for 0.5 min) was increased to 210 °C at 30 °C/min (held at 210 °C for 2 min), then increased to 310 °C at 25 °C/min (held at 310 °C for 3.17 min). Automatic injection of sample (1 μL) was conducted in the split mode. The temperature of both the injector and detector was 300 °C. Quantification of PBDEs was carried out with the internal standard calibration procedure. The congeners in the sample extracts were determined based on their chromatographic retention times relative to the internal standard, PCB-204; 2,2′,3,4,4′,5,6,6′-octachlorobiphenyl (AccuStandard, New Haven, CT, USA).

2.3. QC/QA

During each analysis series (8 samples), quality assurance pooled samples were examined. Within the scope of the analysis, duplicated Na_2SO_4 spiked PBDEs and method blanks were examined parallel to the tissue samples in order to detect potential contamination during sample processing. Method detection limits (MDL) were calculated by the average blanks of each congener plus three times the standard deviation (Table 1). Analytical accuracy was guaranteed through regular analysis of NIST Standard Reference Materials (SRM1945) of organics in whale blubber. Replicate aliquots of dolphin blubber, muscle, and liver samples were analyzed for quality control. All data met the QA/QC specifications. Recoveries measured for the spiked standards ranged between 70% and 101% (Table 1). Total PBDE (ΣPBDE) represents the sum of 17 BDE congeners. Data are presented on a fat-weight basis.

2.4. Statistics

Statistical analyses were performed using Minitab 11.0. Concentrations below the level of detection (Table 1) were treated as zero for further statistical analysis. To compare concentrations among tissues from female and male dolphins, multivariate analysis of variance (MANOVA) was used to compare mean contaminant concentrations between the eight individual samples, including five males and three females. Using contrasts (Turkey-Kramer), individual analyses of variance (Welch's ANOVA for unequal variances) were conducted to determine which compound concentrations were significantly different among tissues. MANOVA was also used to compare concentrations of 13 dominant PBDE congeners among the tissue classes. Relative proportions of individual PBDE congeners to the total PBDEs (pattern of congener) among the tissue types were examined using principal component analysis (PCA).

3. Results and discussion

3.1. PBDE concentrations in pantropical spotted dolphins

Total PBDE (ΣPBDE) concentrations in the stranded pantropical spotted dolphin ranged from 1.74 (female muscle) to 436 ng/g fat (male blubber), with an overall mean of 86.5 ± 125 ng/g fat (Table 2). In general, the variation in the mean concentration of contaminants in marine mammals may be due to the fluctuation in lipid contents and compositions in organisms of different species,

Please cite this article in press as: F.C. Ko, et al., Bioaccumulation of persistent organic pollutants in stranded cetaceans from Taiwan coastal waters, J. Hazard. Mater. (2014), http://dx.doi.org/10.1016/j.jhazmat.2013.12.057