

LEVELS AND TEMPORAL TRENDS OF BROMINATED FLAME RETARDANTS AND ORGANOCHLORINE POPs IN MELON-HEADED WHALES FROM JAPAN

Isobe T^{1*}, Sugimoto R¹, Amano M², Tajima Y³, Yamada TK³, Tanabe S¹

¹ Center for Marine Environmental Studies, Ehime University, Bunkyo cho 2-5, Matsuyama 790-8577, Japan;

² Nagasaki University, Nagasaki, Japan; ³ National Museum of Nature and Science, Tokyo, Japan

Introduction

Total 32 melon-headed whales (*Peponocephala electra*) were mass stranded and died at the coast of Kashima City, Japan in March 2011. Melon-headed whale is an oceanic species and ranging from tropical to subtropical waters in schools of 100-1000 individuals. An adult is about 2.5-3 m long and weighs about 200 kg with lifespan of 20-30 years. They sometimes strand in large number at the coast probably because of their strong relationship between individuals in a school. Some mass mortalities of this species have also been reported on the Pacific Coast of Japan since 1980s though the cause of stranding has never been determined. It is well known that cetaceans accumulate persistent organic pollutants (POPs) in their body through the food web. Because of its persistence, bioaccumulative and toxic characteristics, brominated flame retardants (BFRs) including PBDEs and HBCDs as well as legacy POPs such as PCBs and DDTs are of public concern. Although not much is known on the potential effects of organic contaminants in marine mammals, recent studies demonstrated that POPs and BFRs could disrupt the endocrine systems of marine mammals. Some reports are available on the environmental behavior, fate and ecotoxicological risk of those persistent pollutants¹⁻³, but limited information on the contamination status and temporal variation of those chemicals in oceanic cetaceans is available so far. In this regard, we analyzed organohalogen contaminants including PCBs, DDTs, CHLs, HCHs, HCB, PBDEs and HBCDs in blubber, liver, muscle and brain of melon-headed whales to elucidate the contamination status and body burden. In addition, temporal trends of levels of organohalogen contaminants were also investigated by analyzing archived blubber samples of this species.

Materials and methods

Samples

Thirty-two stranded melon-headed whales (*Peponocephala electra*) were collected from Kashima City, Japan in March 2011 (Figure 1). Fourteen of thirty-two individuals were dissected on site and the rest was transported to the labs (either National Museum of Nature and Science or Ehime University). For analysis of contaminants, blubber, liver, muscle and brain samples were excised from the animals and stored at the Environmental Specimen Bank (es-BANK) of Ehime University at -25 °C until analysis. Age was determined by counting the annual growth layer groups on the teeth of specimen. Biometry including estimated age, sex, maturity status, body length, body weight and tissue weight are summarized in Table 1.

Chemical analysis

Analysis of BFRs (PBDEs and HBCDs), PCBs and organochlorine pesticides (OCPs: DDTs, CHLs, HCB and HCHs) were carried out following previous reports⁴⁻⁶. Briefly, 2-10 g of tissue sample was extracted with hexane/acetone (1:1, v/v) using

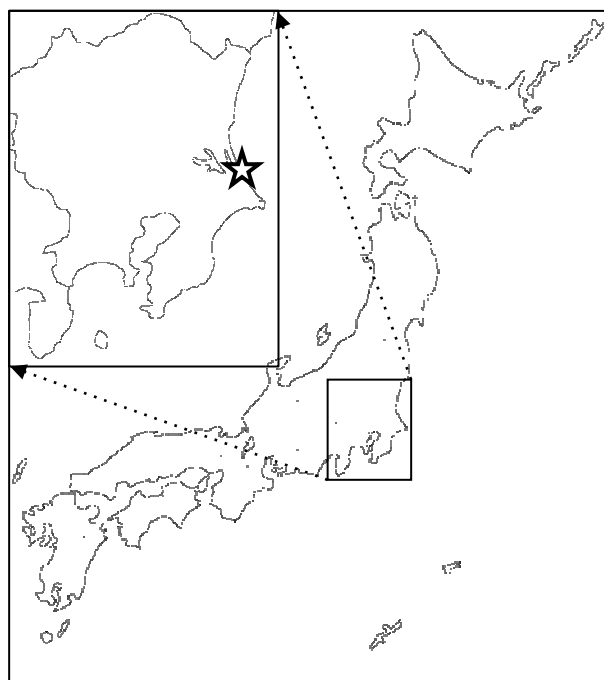


Figure 1. Sampling location

a high-speed solvent extractor. For PCBs, PBDEs and HBCDs analysis, the extract was spiked with surrogates ($^{13}\text{C}_{12}$ -PCBs, $^{13}\text{C}_{12}$ -PBDEs and $^{13}\text{C}_{12}$ -HBCDs) and purified with gel permeation chromatography (GPC) and fractionated with an activated silica gel column chromatography. The fraction containing PCBs and PBDEs was spiked with $^{13}\text{C}_{12}$ -BDE-139 as an internal standard and subjected to GC-MS analysis. The HBCDs fraction was evaporated and spiked with HBCDs- d_{18} prior to LC-MS/MS analysis. For analysis of OCPs including DDTs, HCHs, CHLs, and HCB, another aliquot of the Soxhlet extract was purified and fractionated using a GPC and an activated florisil column. Identification and quantification of OCPs was performed using a GC-ECD without recovery correction. Concentrations of analytes were expressed as ng/g lipid weight unless stated otherwise.

Results and discussion

Contamination status

Table 1. Biometry of melon-headed whales (*Peponocephala electra*) stranded at Kashima Coast, Japan

Sample ID	Age	Sex	Sex Maturity	BL(cm)	BW (kg)	Tissue weight (kg)			
						Blubber (%)	Liver (%)	Muscle (%)	Brain (%)
110306-1		M	Mature	262					
110306-3	2	M	Immature	187					
110306-4	29	M	Mature	255					
110306-5	28	M	Mature	239					
110306-6	27	M	Mature	248					
110306-7		M	Mature	268					
110306-8	13	M	Mature	256					
110306-9	20	M	Mature	242					
110306-11	34	M	Mature	256					
110306-12	19	M	Mature	241					
110306-16	30	M	Mature	252					
110306-17	27	M	Mature	260	232	58 (25)	3.9 (1.7)	114 (49)	1.5 (0.6)
110306-18	29	M	Mature	248	212				
110306-19	6	M	Immature	235	152				
110306-20		M	Immature	244					
110306-21	26	M	Mature	262					
110306-22	15	M	Mature	263	198	52 (26)	3.4 (1.7)	93 (47)	1.6 (0.8)
110306-23	19	M	Mature	252	193				
110306-26	19	M	Mature	250	218.6	50 (23)	3.9 (1.8)	85 (39)	1.4 (0.6)
110306-27	30	M	Mature	270	249.8	64 (26)	4.7 (1.9)	89 (36)	1.4 (0.5)
110306-28	24	M	Mature	256	226	62 (28)	4.0 (1.8)	134 (59)	1.4 (0.6)
110306-31	26	M	Mature	250	210				
110306-2	19	F	Mature	246					
110306-10	19	F	Mature	239					
110306-13	15	F	Mature	230					
110306-14	14	F	Mature	252					
110306-15	14	F	Mature	250					
110306-24	33	F	Mature	238					
110306-25	11	F	Immature	252	151.5	44 (29)	2.4 (1.6)	90 (59)	1.3 (0.8)
110306-29	7	F	Immature	231	133	56 (42)	2.3 (1.7)	38 (28)	1.2 (0.9)
110306-30		F	Mature	252	183				
110306-32	38	F	Mature	248	164.4	36 (22)	4.1 (2.5)	68 (41)	1.4 (0.9)

All the targeted organohalogen contaminants were detected in all 32 analyzed blubber of melon-headed whales, indicating this species also accumulates those persistent organic pollutants in their body. Among target compounds, DDTs (male: 3500-26000 ng/g lw, female: 950-13000 ng/g lw) were the predominant contaminants followed by PCBs (male: 4700-16000 ng/g lw, female: 940-8100 ng/g lw), CHLs (male: 1600-5600 ng/g lw, female: 260-2600 ng/g lw), HBCDs (male: 300-900 ng/g lw, female: 160-660 ng/g lw), PBDEs (male: 200-540 ng/g lw, female: 46-370 ng/g lw), HCB (male: 170-410 ng/g lw, female: 46-270 ng/g lw) and HCHs (male: 140-310 ng/g lw, female: 34-280 ng/g lw). Ranges of concentrations were within the previous studies reporting the levels of organohalogens in cetaceans from Asian coasts^{2, 4, 7-12}. Levels in males were greater than those in females ($p < 0.01$) for all the analytes, suggesting the possibility of maternal and lactation transfer of contaminants from adult female to calf.

Accumulation feature and temporal trend

Lipid weight basis concentrations of organohalogen contaminants showed no significant difference among the analyzed tissues, except for brain, which showed lower levels probably due to presence of blood-brain barrier. Retrospective analysis was also performed using archived blubber samples of male adult melon-headed whales collected in 1982, 2001 and 2006 and stored in es-BANK of Ehime University (Figure 2). Slightly, but significant, decreasing trends during last 3 decades were observed for concentrations of PCBs and DDTs while other pesticides didn't show the significant trends. On the other hand, substantial increase of PBDEs and HBCDs were observed, suggesting growing consumption in Japan and other Asian countries during the study period. These changes in BFRs levels were consistent with the trends of BFRs market demands in Japan. As a result of the regulation on some PBDE products from the Japanese market in 1990s, concentrations of HBCDs are higher than those of PBDEs in recent years, reflecting increasing usage of HBCDs over PBDEs. Since environmental levels are increasing and BFRs are high production volume compounds in Asia, further studies on source identification and ecotoxicological risk assessment are warranted.

Acknowledgements

Financial support was provided by Grants-in-Aid for Scientific Research (A: 25257403, B: 25281008, Challenging Exploratory Research: 24651010), Global COE Program of the Japanese Ministry of Education, Science, Sports, Culture and

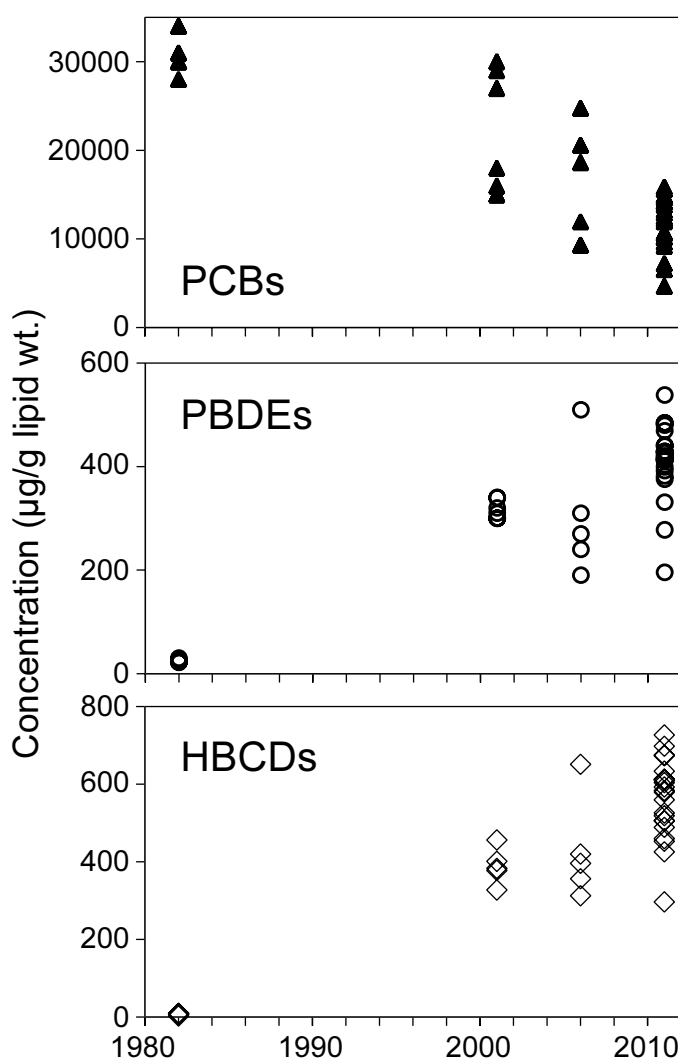


Figure 2. Temporal trends of PCBs, PBDEs and HBCDs in blubber of melon-headed whales (*Peponocephala electra*) from Japan coasts

Technology (MEXT) and Japan Society for the Promotion of Science (JSPS) and the Environment Research and Technology Development Fund (5ZRFc-1201) of the Japanese Ministry of the Environment.

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