CHLORINATED AND BROMINATED PERSISTENT ORGANIC POLLUTANTS IN MASS STRANDED STRIPED DOLPHINS (*STENELLA COERULEOALBA*) FROM MINAMISATSUMA, JAPAN

Isobe T[1,2]*, Kume N, Amano M[3], Yamada TK[4], Tajima Y[4], Tanabe S[1]

[1]Ehime University, Bunkyo cho 2-5, Matsuyama 790-8577, Japan; [2]National Institute for Environmental Studies, Onogawa 16-2, Tsukuba 305-8506, Japan; [3]Nagasaki University, Bunkyo cho 1-14, Nagasaki 852-8521, Japan; [4]National Museum of Nature and Science, Amakubo 4-1-1, Tsukuba 305-0005, Japan

Introduction

Striped dolphin (*Stenella coeruleoalba*) is an oceanic species and ranging from tropical to temperate offshore waters all over the world. They live in schools of tens to hundreds individuals and sometimes are subjected to the local coastal whaling in Japan. The conservation status in IUCN Red List is assigned as Least Concern, indicating risk of extinction of this species is low. An adult is about 2.4-2.6 m long and weighs about 150-160 kg with lifespan of 50-60 years. They are higher-level consumers in the marine food web and feeding on cephalopods, crustaceans and fish. Because of their long lifespan and feeding habits, they accumulate persistent lipophilic chemicals in their body. Some mass mortalities, more than 1,000 individuals, of this species have been reported in the Mediterranean since the 1980s, while such sorrowful event barely occur in Japanese coasts. A part of the cause of the mass mortality in the Mediterranean was suspected to environmental pollution since extremely high levels of organochlorine contaminants, e.g., PCBs and DDTs, were detected[1-3]. Because of their persistent, bioaccumulative and toxic characteristics, environmental contamination by persistent organic pollutants (POPs) is of public concern. POPs consist of dirty dozen (legacy POPs) and some other recently listed contaminants including brominated flame retardants (BFRs). Although not many studies have been conducted on the potential adverse effects of POPs on marine mammals, recent studies demonstrated that legacy 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 pollutants [4-6], 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 of striped dolphins stranded at the Japanese coast to elucidate the contamination status. In addition, temporal trends of levels of organohalogen contaminants were also investigated by comparing with archived blubber samples of this species.

Materials and methods

Sample collection

Total 31 striped dolphins were mass stranded and 29 individuals died at the coast of Minami-Satsuma City, Kagoshima, Japan in 26 April 2013. Among them, 17 individuals were transported to es-BANK of Ehime University and 10 individuals were to National Museum of Nature and Science (Tsukuba) and stored in freezing rooms at –25 or –20˚C, respectively. All the specimens (n = 27, male = 10, female = 17) were dissected and blubber, muscle, liver, kidney and brain were excised from the animals and archived in es-BANK. In this study, blubber was used to determine lipophilic contaminants.

Chemical analysis

Analysis of PCBs, organochlorine pesticides (OCPs: DDTs, CHLs, HCB and HCHs) and BFRs (PBDEs and HBCDs) were carried out following the previous reports[7-9]. Briefly, 2-3 g of blubber sample was extracted with 300 mL of hexane/acetone (1:1, v/v) mixture using a high-speed solvent extractor (Mitsubishi Chemical, SE-100). For PCBs, OCPs, PBDEs and HBCDs analysis, the extract was spiked with surrogates ($^{13}C_{12}$-PCBs, $^{13}C_{12}$-PBDEs and $^{13}C_{12}$-HBCDs), purified with gel permeation chromatography (GPC) and fractionated with an activated silica gel column chromatography. The fraction containing PCBs, PBDEs and OCPs was spiked with

$^{13}C_{12}$-BDE-139 as an internal standard and subjected to GC-MS or GC-MS/MS determination. The HBCDs fraction was evaporated and spiked with HBCDs-d_{18} as internal standards prior to LC-MS/MS analysis. Concentrations of analytes were expressed as ng/g lipid weight unless stated otherwise. Results were compared with our previous report to develop the temporal variation and find the trend during this decade [10].

Results and discussion

Contamination status

All the targeted organohalogen contaminants were detected in all 27 analyzed blubber of striped dolphins, indicating this species accumulates those POP chemicals in their body (Table 1). Among target compounds, DDTs (male: 9,300-876,000 ng/g lw, female: 870-57,000 ng/g lw) were the predominant followed by PCBs (male: 2,200-10,000 ng/g lw, female: 280-1,000 ng/g lw), CHLs (male: 2200-9300 ng/g lw, female: 200-8,800 ng/g lw), HBCDs (male: 690-1,700 ng/g lw, female: 160-1,600 ng/g lw), PBDEs (male: 280-1,300 ng/g lw, female: 50-920 ng/g lw), HCHs (male: 180-580 ng/g lw, female: 44-460 ng/g lw) and HCB (male: 190-550 ng/g lw, female: 41-350 ng/g lw). Ranges of concentrations were within the previous studies reporting the levels of organohalogens in cetaceans from Asian coasts [5, 7, 10-15]. Levels in males were greater than those in females ($p < 0.05$) for all the analytes (Fig. 1), suggesting the possibility of maternal and lactational transfer of contaminants from adult female to calf.

Temporal trend study

To develop the temporal variation in the levels of analytes, results of this study was compared with our previous data on the concentrations in blubber of striped dolphins collected in 1978, 79, 86, 92 and 2003 and stored in es-

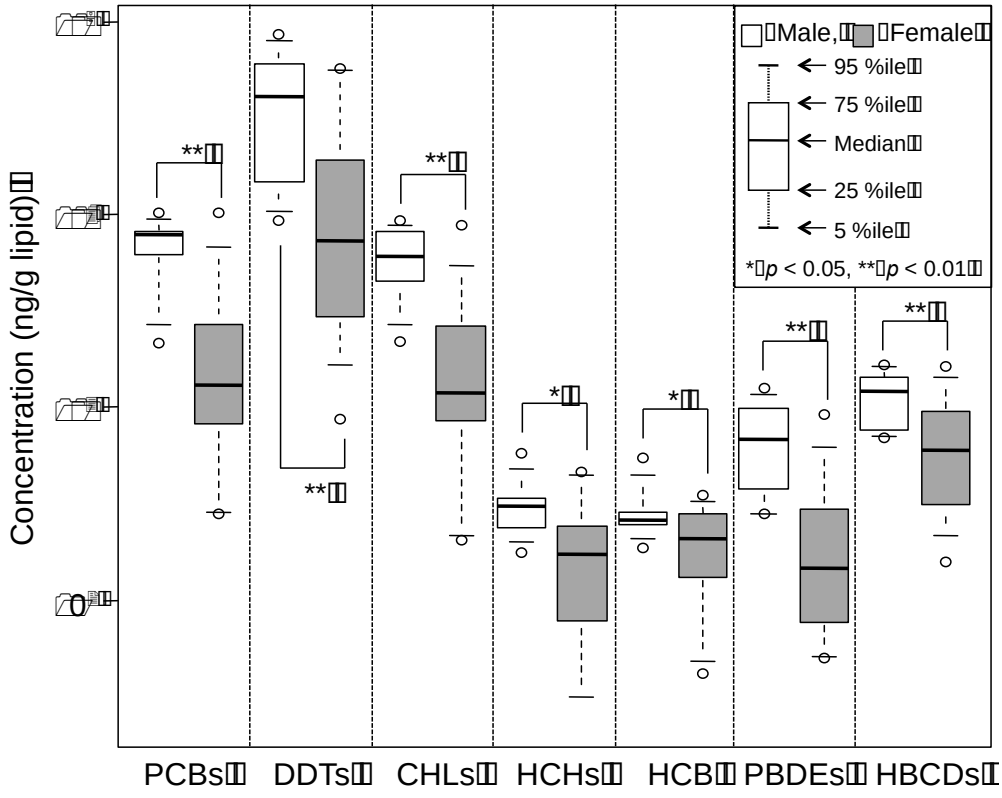

Figure 1. Concentration ranges of PCBs, DDTs, CHLs, HCHs, HCB, PBDEs and HBCDs in blubber of striped dolphins (*Stenella coeruleoalba*) mass stranded at Minami-Satsuma coast, Japan.

BANK of Ehime University [10]. Concentrations of PCBs, DDTs, HCHs and HCB in adult male blubber showed significant decreasing trends during the research period ($p < 0.05$), while CHLs didn't show obvious trend. Because the use of POPs was restricted worldwide, these chemicals showed decreasing 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 BFR 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.

Table 1. Body length, lipid content and concentrations of organohalogen contaminants in blubber of mass-stranded striped dolphins (*Stenella coeruleoalba*) from Minami Satsuma

Sample ID	Gender	Body length	Lipid content	Concentration (ng/g lipid)						
		(cm)	(%)	PCBs	DDTs	CHLs	HCHs	HCB	PBDEs	HBCDs
140426SC01	F	224	61	6000	12000	4600	400	350	450	990
140426SC02	F	224	42	830	1900	520	70	120	65	310
140426SC03	F	220	57	2300	7300	2300	160	230	170	600
140426SC04	M	244	63	6600	9300	4600	180	190	370	720
140426SC05	F	241	36	710	3000	850	90	130	76	480
140426SC06	F	227	53	280	870	200	24	50	50	160
140426SC07	F	224	51	2700	6600	2700	240	280	300	730
140426SC08	M	228	51	8100	15000	6200	230	290	720	690
140426SC09	M	242	44	8200	22000	6000	240	260	530	870
140426SC10	M	232	42	3300	12000	3300	320	230	280	760
140426SC11	M	235	36	10000	60000	7200	340	280	810	1600
140426SC12	F	215	55	10000	57000	8800	460	320	920	1600
140426SC13	M	205	46	2200	25000	2200	280	260	280	1100
140426SC14	F	229	56	280	1900	220	33	41	53	260
140426SC15	F	231	37	3100	32000	3300	430	280	390	1300
140426SC16	F	221	45	1400	22000	1400	240	180	170	680
140426SC17	M	241	31	6200	57000	6000	300	260	650	1300
140426SC18	M	230	33	7800	87000	9300	580	550	1300	1300
140426SC19	F	229	50	1100	19000	1200	180	210	130	550
140426SC20	M	226	53	8500	61000	8400	350	250	990	1400
140426SC21	F	231	34	1300	14000	900	78	66	230	1400
140426SC22	F	225	47	960	15000	1100	220	210	140	660
140426SC23	M	251	43	8300	74000	8300	340	330	1100	1700
140426SC24	F	226	42	4300	57000	4400	440	280	550	950
140426SC25	F	230	34	1600	5500	1900	170	220	150	540
140426SC26	F	229	59	480	2000	530	74	140	51	230
140426SC27	F	223	46	870	3500	930	110	180	82	300

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