Arch. Environ. Contam. Toxicol. 39, 398–410 (2000)
DOI: 10.1007/s002440010121

ARCHIVES OF
Environmental
Contamination
and Toxicology

Isomer-Specific Accumulation and Toxic Assessment of Polychlorinated Biphenyls, Including Coplanar Congeners, in Cetaceans from the North Pacific and Asian Coastal Waters

T. B. Minh,[1] H. Nakata,[2] M. Watanabe,[1] S. Tanabe,[1] N. Miyazaki,[3] T. A. Jefferson,[4] M. Prudente,[5] A. Subramanian[6]

[1] Center for Marine Environmental Studies, Ehime University, Tarumi 3-5-7, Matsuyama 790-8566, Japan
[2] Department of Environmental Science, Kumamoto University, Kurokami 2-39-1, Kumamoto 860-8555, Japan
[3] Otsuchi Marine Research Center, The Ocean Research Institute, The University of Tokyo, Akahama, Otsuchi-cho, Iwate 028-1102, Japan
[4] Southwest Fisheries Science Center, National Marine Fisheries Service, NOAA, P.O. Box 271, La Jolla, California 92038, USA and Ocean Park Conservation Foundation, Ocean Park, Aberdeen, Hong Kong
[5] Science Education Department, De La Salle University, 2401 Taft Avenue, 1004 Manila, Philippines
[6] Centre of Advanced Study in Marine Biology, Annamalai University, Parangipettai 608502, India

Received: 7 September 1999/Accepted: 3 May 2000

Abstract. To elucidate the global distribution and toxicological impacts of polychlorinated biphenyls (PCBs) on cetaceans, the present study determined the concentrations of individual PCB congeners, including toxic non-*ortho* (IUPAC Nos. 77, 126, 169) and mono-*ortho* (IUPAC Nos. 105, 118, 156) coplanar congeners, in the blubber of 10 species of adult male odontocetes collected from several locations in the North Pacific Ocean and along coastal waters of Japan, Hong Kong, the Philippines, and India during 1985–1997. Total PCB concentrations in cetaceans from temperate and cold waters were higher than those in cetaceans from tropical regions. Residue levels were found to be the highest in Fraser's dolphins collected off Kii Peninsula, Japan, and hump-backed dolphins from Hong Kong, reflecting serious marine pollution by PCBs in industrialized Asian countries. Penta- and hexa-chlorobiphenyls were the predominant PCB congeners, accounting for about 70% of the total PCBs. 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin equivalents (TEQs) of non- and mono-*ortho* coplanar PCBs in the blubber of cetaceans ranged from 36 (in spinner dolphins from the Philippines) to 510 pg/g wet weight (in hump-backed dolphins from Hong Kong). Toxic evaluation of coplanar PCBs using the TEQ concept indicates an greater impact on cetaceans from mid-latitudes. Toxicity contribution of mono-*ortho* congener IUPAC 118 was prominent in species from high latitude oceans, such as the Bering Sea and the North Pacific, whereas non-*ortho* congener IUPAC 126 accounted for the highest contribution in cetaceans from lower latitude regions, such as the Philippines and India. The estimated TEQ concentrations in the blubber of some cetacean species, such as northern right whale dolphin and Pacific white-sided dolphin from the northern North Pacific, Dall's porpoise from the Japan Sea, striped dolphin off Sanriku and Fraser's dolphin off Kii Peninsula, Japan, hump-backed dolphin and finless porpoise from Hong Kong, exceeded the levels associated with immunosuppression in harbour seals.

Correspondence to: S. Tanabe

Polychlorinated biphenyls (PCBs) are persistent, highly bioaccumulative, and toxic contaminants. They consist of 209 isomers and congeners exhibiting different physicochemical properties and biological activities, which results in complex environmental distributions and toxic responses (Tanabe 1988; Safe 1994; Giesy and Kannan 1998). Among a number of toxic man-made chemicals, PCBs are some of the most extensively studied contaminants in terms of environmental contamination and toxicological impact. Due to worldwide usage in huge quantities, PCBs have been detected in a variety of environmental compartments, and their residue levels were found to be significantly higher than those of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), which are known to have highly toxic and similar biological effects to coplanar PCBs (Tanabe *et al.* 1987a; Kannan *et al.* 1989a).

Our recent comprehensive surveys on global contamination by persistent organochlorines (OCs) have revealed that large quantities of OCs used in tropical regions are released into the atmosphere and redistributed via long-range atmospheric transport on a global scale (Iwata *et al.* 1993, 1994; Tanabe *et al.* 1994). In this context, it was also indicated that open ocean may serve as a final sink for such chemicals, and, therefore, toxic threat by persistent OCs to marine organisms is a matter of great concern. Being top predator of

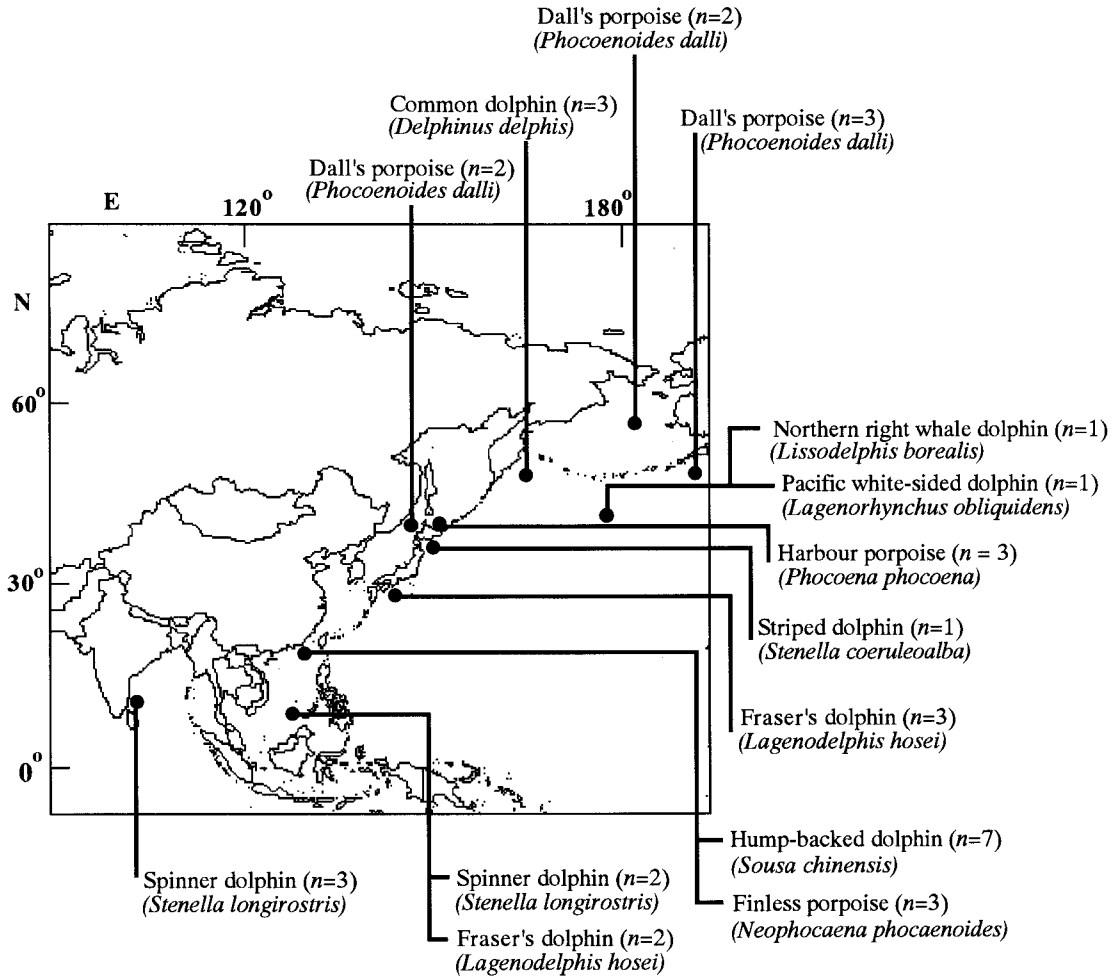

Fig. 1. Map showing geographical sampling locations of cetaceans from the North Pacific and Asian coastal waters. Values in parentheses indicate number of samples analyzed

marine food chain, marine mammals, particularly cetaceans, are considered to be the most vulnerable animals to the long-term toxic effects by persistent OCs (Tanabe and Tatsukawa 1992; Colborn and Smolen 1996). Elevated concentrations of PCBs, including highly toxic coplanar congeners, have been reported in tissues of marine mammals and birds, and these levels have been suspected to be linked to a series of mass mortalities of marine mammals that occurred during the last decade. The linkage of elevated PCB residues and disease includes the epizootic in harbor seals from the Baltic Sea and the North Sea (Heide-Jorgesen *et al.* 1992; Storr-Hansen and Spliid 1993), beluga whales from the St. Lawrence River (Martineau *et al.* 1987), diseased striped dolphins from the Mediterranean Sea (Kannan *et al.* 1993; Aguilar and Borrell 1994), and embryonic abnormalities in waterbirds from the Great Lakes (Yamashita *et al.* 1993). Chronic exposure to toxic man-made chemicals, particularly coplanar PCBs and butyltin compounds, may be responsible for immunosuppression in these marine mammals (Swart *et al.* 1994; Ross *et al.* 1995; Kannan *et al.* 1993, 1997, 1998). Despite numerous studies of the status of contamination and biological effects of PCBs, knowledge of their distribution, fate, and toxicological impacts on a global scale is scarce. Moreover, little is known about PCB isomer accumulation and TEQs of coplanar congeners in cetaceans in a wide geographical range, such as the North Pacific Ocean and Asian coastal waters, particularly the tropical region.

In this study, we report the concentrations of individual PCB congeners and their 2,3,7,8-tetrachlorodibenzo-*p*-dioxin equivalents (TEQs) in 10 species of adult male odontoceti cetaceans collected from various locations in the North Pacific and along coastal waters of Japan, the Philippines, and India. The present study aims to understand isomer-specific bioaccumulation of PCBs in the blubber of various species of odontoceti cetaceans from different locations in the North Pacific and Asian coastal waters and to evaluate possible toxicological impacts of highly toxic coplanar biphenyls on cetaceans in a global scale.

Materials and Methods

Blubber samples were taken from 10 species of adult male odontoceti cetaceans collected from different locations of the North

Table 1. Comparison of total PCB concentrations and TEQs of non- and mono-*ortho* coplanar PCBs in cetaceans from various regions[a]

Species	Location	Survey Year	n	Total PCBs (μg/g wet weight)	Total TEQs (pg/g wet weight)	Reference
Dall's porpoise	Bering Sea	1985	2	13 (11–14)[b]	82	present study
Dall's porpoise	Northeastern North Pacific	1987	3	19 (16–21)	150	present study
Common dolphin	Northwestern North Pacific	1987	3	22 (19–26)	110	present study
Harbor porpoise	Hokkaido, Japan	1993	3	8.0 (4.1–12)	100	present study
Dall's porpoise	Japan Sea	1989	2	34 (33–34)	290	present study
Northern right whale dolphin	Northern North Pacific	1991	1	30	190	present study
Pacific white-sided dolphin	Northern North Pacific	1991	1	27	240	present study
Striped dolphin	Off Sanriku, Japan	1992	1	37	280	present study
Fraser's dolphin	Off Kii Peninsula, Japan	1991	3	51 (45–57)	400	present study
Hump-backed dolphin	Hong Kong	1993–1997	7	31 (13–50)	510	present study
Finless porpoise	Hong Kong	1993–1997	3	20 (5.9–48)	400	present study
Spinner dolphin	Mindanao Sea, Philippines	1996	2	2.5 (2.4–2.6)	36	present study
Fraser's dolphin	Mindanao Sea, Philippines	1996	2	6.2 (3.8–8.6)	45	present study
Spinner dolphin	Bay of Bengal, India	1990	3	2.2 (1.6–3.0)	69	present study
Dall's porpoise	Northern North Pacific	1980–1985	5	8.6 (1.0–18)	61	Kannan *et al.* (1989a)
Finless porpoise	Seto Inland Sea, Japan	1985	1	320	1,400	Kannan *et al.* (1989a)
Baird's beaked whale	Pacific coast of Japan	1985	3	2.3 (1.8–2.8)	55	Kannan *et al.* (1989a)
Killer whale	Pacific coast of Japan	1986	3	370 (350–410)	2,800	Kannan *et al.* (1989a)
Harbor porpoise	Black Sea	1993	8	22 (13–34)	170	Tanabe *et al.* (1997)
Striped dolphin	Western Mediterranean Sea	1990	10	390 (94–670)	3,300	Kannan *et al.* (1993)
Bottlenose dolphin	Italian coastal waters	1992	8	590 (90–1,400)	2,500	Corsolini *et al.* (1995)
Risso's dolphin	Italian coastal waters	1992	2	320 (20–610)	3,100	Corsolini *et al.* (1995)
Harbor porpoise	Puck Bay, Baltic Sea	1989–1990	3	31 (23–42)	160	Falandysz *et al.* (1994)
Beluga whale	St. Lawrence river	1987–1990	5	160	890	Muir *et al.* (1996)
Bottlenose dolphin	Florida coast, USA	1989–1994	6	92 (1.6–290)	660	Watanabe *et al.* (2000)
Atlantic spotted dolphin	Florida coast, USA	1989–1994	2	13 (7.9–19)	100	Watanabe *et al.* (2000)
Pygmy sperm whale	Florida coast, USA	1989–1994	2	0.56 (0.29–0.83)	18	Watanabe *et al.* (2000)
Killer whale	British Columbia coast	1986–1989	6	22 (8.6–56)	380[c]	Jarman *et al.* (1996)
False killer whale	British Columbia coast	1987–1989	3	40 (34–46)	360[c]	Jarman *et al.* (1996)
Risso's dolphin	British Columbia coast	1988	1	1.7	77[c]	Jarman *et al.* (1996)
Dall's porpoise	British Columbia coast	1987–1988	3	4.5 (0.47–43)	380[c]	Jarman *et al.* (1996)
Harbor porpoise	British Columbia coast	1987–1989	6	8.4 (4.4–16)	290[c]	Jarman *et al.* (1996)

[a] TEQs were calculated using TEF values cited from Van den Berg *et al.* (1998).
[b] Range concentration.
[c] TEQs were calculated for only non-*ortho* coplanar congeners.

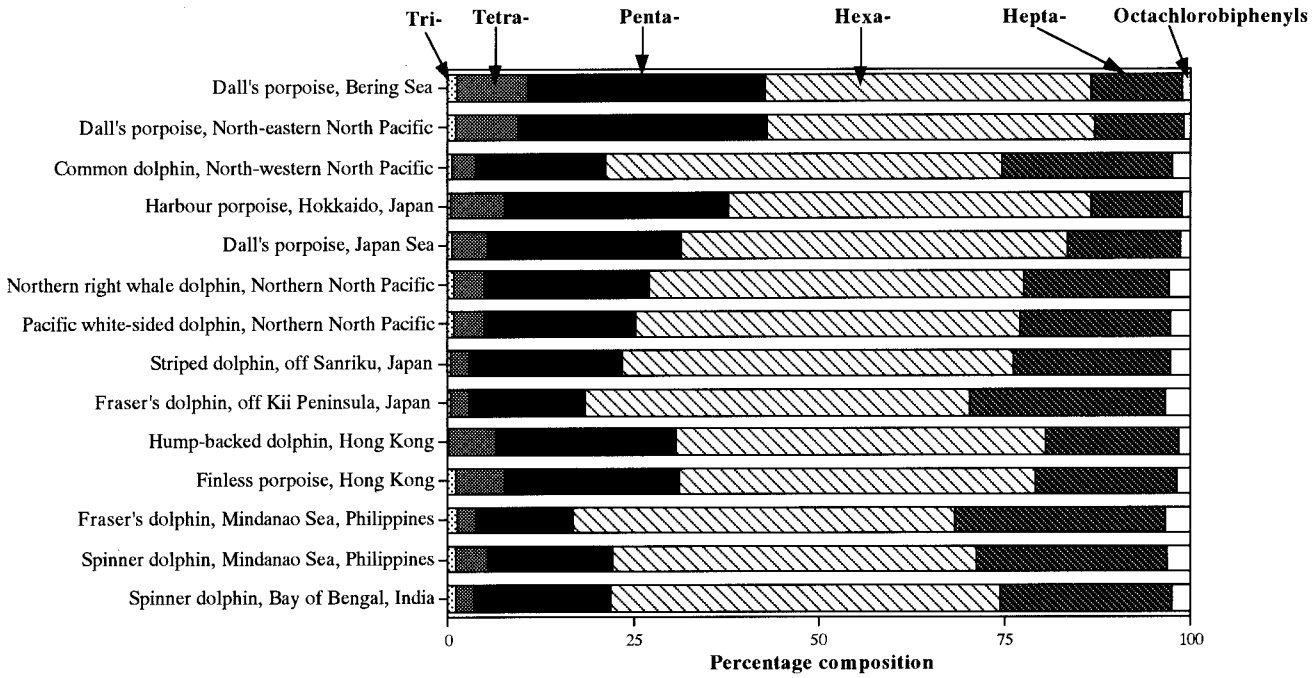

Fig. 2. Percentage composition of PCB congeners in the blubber of cetaceans from the North Pacific and Asian coastal waters

Pacific and along coastal waters of Japan, the Philippines, and India during 1985–1997. Data of two species, Indo-Pacific hump-backed dolphin and finless porpoise, were also included based on our previous study (Minh *et al.* 1999). Sampling locations of cetacean are shown in Figure 1. Blubber samples were obtained from three sources: (1) the fresh strandings along the coastlines, (2) accidental catches by fishermen, and (3) specimens collected by Whaling for Commercial and Scientific Purposes that were accepted by an international convention for the regulation of whaling. In the framework of our research, only those species with large population sizes were collected, and endangered species were ruled out. Since the purpose of this study is to discuss PCB accumulation in cetaceans on a global scale, factors influencing organochlorine concentrations, such as reproductive status, should be minimized. For this reason, only adult male animals were subjected for analysis. Blubber samples were taken from these individuals and immediately after dissection, samples were frozen in clean plastic bags, transported to the laboratory and stored at −20°C until analysis.

The analytical procedure for PCBs and non-*ortho* coplanar congeners (IUPAC Nos. 77, 126, 169) was similar to that described previously (Wakimoto *et al.* 1971; Tanabe *et al.* 1987b). Briefly, 4–5 g of blubber was homogenized with anhydrous Na_2SO_4 and Soxhlet extracted for 8 h. Extractable lipid content was gravimetrically determined from an aliquot of the extract. An aliquot of the concentrated extract was refluxed in 1 M KOH in ethanol for 1 h, and the solution was then transferred to a separatory funnel containing hexane and hexane-washed water. After partitioning, the hexane layer was concentrated and cleaned up on 1.5 g of silica gel (Wako-gel S-1, Wako Chemical Co., Japan) packed on a glass column. PCB congeners were eluted with 200 ml hexane. The hexane was then concentrated to 6 ml, and an aliquot (1 ml) was taken and treated with 5% fuming sulfuric acid and rinsed with hexane-washed water. The remaining 5 ml of hexane was passed through a glass column (5 mm ID) packed with 0.125 g activated charcoal (Wako) for the separation of non-*ortho* coplanar congeners. The first fraction eluted with 100 ml of 20% dichloromethane in hexane containing *ortho*-chlorine-substituted PCBs and other xenobiotics that interfere with the determination of non-*ortho* congeners, was discarded. The second fraction eluted with 100 ml of benzene:ethyl acetate (1:1) containing non-*ortho* coplanar PCBs was microconcentrated and residues were reconstituted into 5 ml of hexane. This hexane was treated with 5% fuming sulphuric acid and hexane-washed water. The final solutions were microconcentrated, if necessary, and injected into a gas chromatograph with a mass selective detector (GC-MSD) for quantification.

Quantification of PCB congeners as well as non-*ortho* coplanar analogues was carried out using a GC-MSD (Hewlett-Packard 5890 Series II) coupled with a MS (Hewlett-Packard 5972 Series) having an electron impact (EI) at 70 eV. The GC column employed was DB-1 (J&W Scientific Inc., USA) fused silica capillary (0.25 mm × 30 m) coated with 100% dimethylpolysiloxane at 0.25 μm film thickness. The column oven temperature was programmed from 70 to 160°C at a rate of 20°C/min, held for 20 min, and then to 260°C at a rate of 2°C/min, held for 30 min. Helium was used as a carrier gas. The injector and ion source temperatures were kept at 250 and 280°C, respectively. An equivalent mixture of Kanechlors 300, 400, 500, and 600 was used as a standard for quantification. Concentrations of individual PCBs were quantified from the peak area of the sample to that of the corresponding external standard. PCBs homologues were determined by selective ion monitoring. Data was acquired by a Hewlett-Packard 5972C data system, in which cluster ions were monitored at *m/z* 254 and 256, 290 and 292, 324 and 326, 358 and 360, 392 and 394, and 428 and 430 for tri-, tetra-, penta-, hexa-, hepta-, and octachlorobiphenyls, respectively. For the analysis of non-*ortho* PCBs, M^+ and $(M + 2)^+$ cluster ions were monitored at *m/z* 290 and 292, 324 and 326, and 358 and 360 for IUPAC Nos. 77, 126, and 169, respectively.

Recoveries of total PCBs and non-*ortho* coplanar congeners were examined by spiking 3.0 μg of Kanechlor standard and 90.2, 91, and 30.4 ng of IUPAC Nos. 77, 126, and 169 standards to corn oil. The recoveries ranged from 100–105% for total PCBs, 93 ± 6.5% for IUPAC 77, 96 ± 7.0% for IUPAC 126, and 93 ± 0.7% for IUPAC 169. PCB congeners are referred by their IUPAC numbers throughout the manuscript.

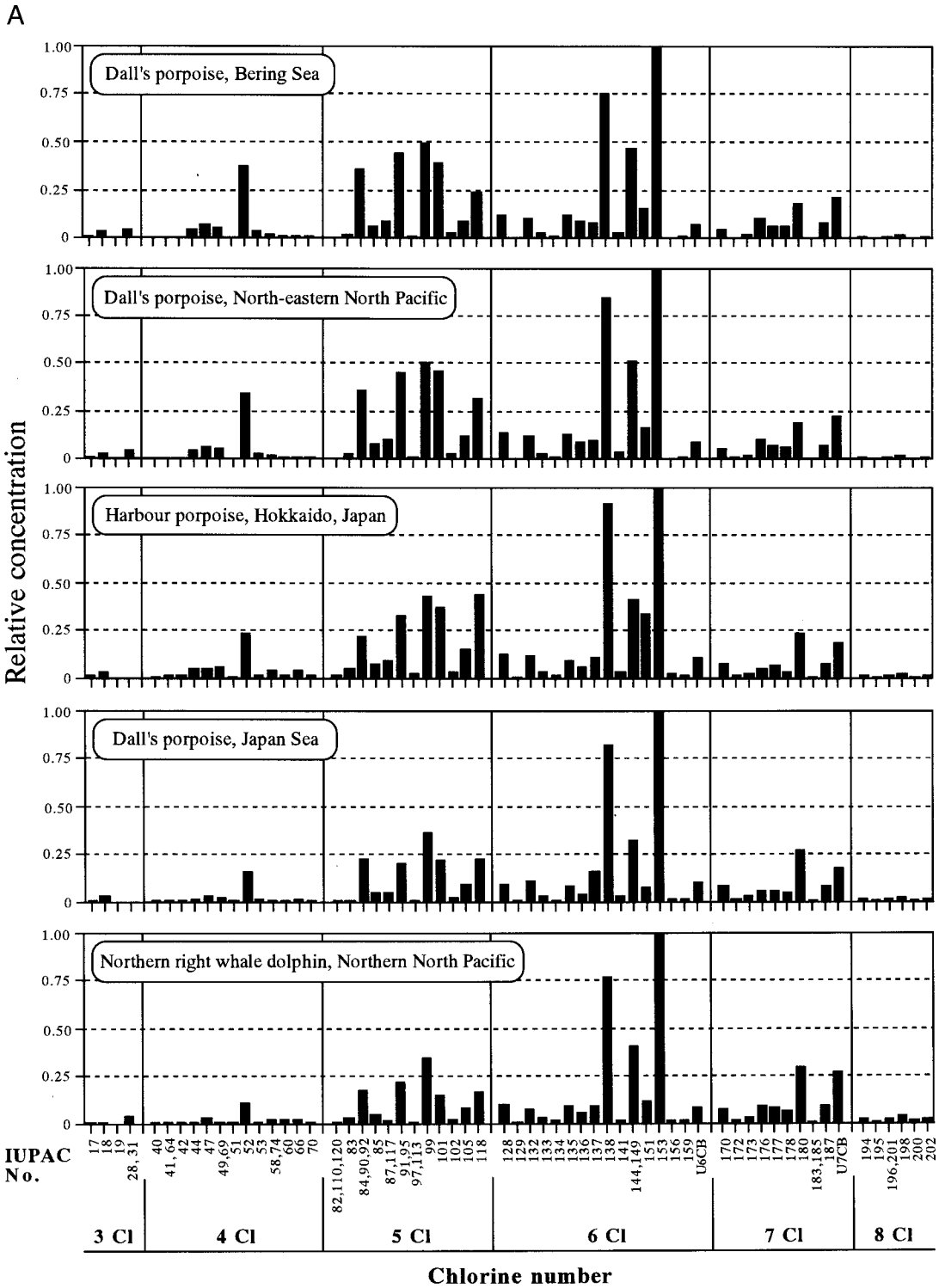

Fig. 3. A: PCB isomer and congener compositions in the blubber of cetaceans from the North Pacific and Asian coastal waters. B: PCB isomer and congener compositions in the blubber of cetaceans from the North Pacific and Asian coastal waters. Vertical bars represent concentrations of individual congeners relative to the most abundant congener (IUPAC No. 153), which was treated as 1.0

A procedural blank was analyzed with every set of six samples to check for interfering compounds to correct sample values, if necessary. For quality assurance and quality control, our laboratory participated in the Intercomparison Exercise for Persistent Organochlorine Contaminants in Marine Mammal Blubber organized by the National Institute of Standards and Technology (NIST) and Marine Mammal Health and Stranding Response Program of the National Oceanic and Atmospheric Administration's National Ma-

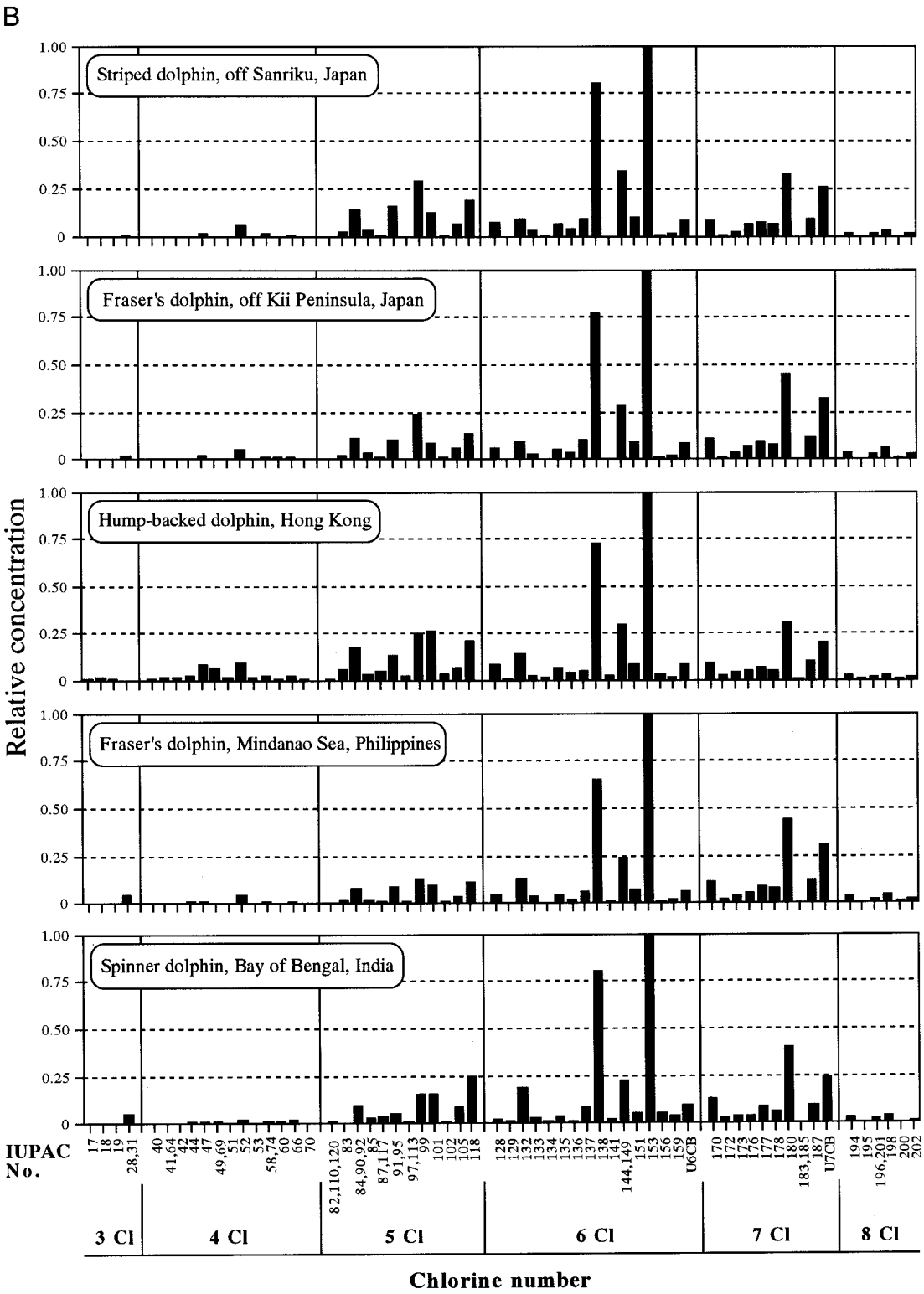

Fig. 3. Continued.

rine Fisheries Service (NOAA/NMFS). Standard reference material SRM 1945 was analyzed for selected PCB congeners and persistent organochlorines. Reliable results were obtained by comparison of generated data from our laboratory with those from material reference values.

Results and Discussion

Total PCB Residue Levels

Total PCB concentrations found in the blubber of cetaceans are given in Table 1. Residue levels ranged from 2.2 (in spinner

Table 2. Concentrations (wet weight) of non- and mono-*ortho* coplanar congeners and their 2,3,7,8-TCDD toxic equivalents (TEQs) in cetaceans from the North Pacific and Asian coastal waters

	Species	Dall's Porpoise		Dall's Porpoise		Common Dolphin	
	Location	Bering Sea		Northeastern North Pacific		Northwestern North Pacific	
	n	2		3		3	
	Lipid (%)	87 (84–89)		86 (95–88)		67 (64–68)	
PCB Congener [IUPAC No.]	TEF*	Conc. (ng/g)	TEQs (pg/g)	Conc. (ng/g)	TEQs (pg/g)	Conc. (ng/g)	TEQs (pg/g)
Non-*ortho*							
IUPAC No. 77	0.0001	0.72 (0.72–0.72)	0.07 (0.07–0.07)	1.1 (0.87–1.3)	0.11 (0.09–0.13)	0.86 (0.55–1.4)	0.09 (0.06–0.14)
IUPAC No. 126	0.1	0.18 (0.17–0.19)	18 (17–19)	0.26 (0.21–0.32)	26 (21–32)	0.23 (0.15–0.36)	23 (15–36)
IUPAC No. 169	0.01	0.17 (0.14–0.19)	1.7 (1.4–1.9)	0.19 (0.13–0.23)	1.9 (1.3–2.3)	0.32 (0.21–0.53)	3.2 (2.1–5.3)
Mono-*ortho*							
IUPAC No. 105	0.0001	150 (150–150)	15 (15–15)	310 (246–360)	31 (24–36)	160 (120–190)	16 (12–19)
IUPAC No. 118	0.0001	420 (400–430)	42 (40–43)	800 (660–900)	80 (66–90)	450 (340–520)	45 (34–52)
IUPAC No. 156	0.0005	9.4 (9.3–9.4)	4.6 (4.6–4.7)	21 (14–29)	11 (7.0–15)	35 (26–40)	18 (13–20)
Total TEQs			81		150		110

	Species	Striped Dolphin		Fraser's Dolphin		Hump-backed Dolphin	
	Location	off Sanriku, Japan		off Kii Peninsula, Japan		Hong Kong	
	n	1		3		7	
	Lipid (%)	50		70 (61–78)		46 (31–76)	
PCB congener (IUPAC No.)	TEF*	Conc. (ng/g)	TEQs (pg/g)	Conc. (ng/g)	TEQs (pg/g)	Conc. (ng/g)	TEQs (pg/g)
Non-*ortho*							
IUPAC No. 77	0.0001	1.1	0.11	3.6 (2.4–5.2)	0.36 (0.24–0.52)	9.1 (3.6–19)	0.91 (0.36–1.9)
IUPAC No. 126	0.1	0.43	43	1.3 (0.89–2.0)	130 (89–200)	2.1 (1.1–2.9)	210 (110–290)
IUPAC No. 169	0.01	0.47	4.7	1.7 (1.3–2.4)	17 (13–24)	0.62 (0.19–0.99)	6.2 (1.9–9.9)
Mono-*ortho*							
IUPAC No. 105	0.0001	480	48	570 (490–640)	57 (49–64)	440 (290–590)	44 (29–59)
IUPAC No. 118	0.0001	1,300	130	1,300 (1,200–1,400)	130 (120–140)	1,500 (1,100–2,000)	150 (110–200)
IUPAC No. 156	0.0005	110	55	130 (120–140)	65 (60–67)	190 (90–290)	95 (45–150)
Total TEQs			280		400		510

dolphins from India) to 51 μg/g wet weight (in Fraser's dolphins off Kii Peninsula). Generally, cetaceans inhabiting temperate and cold waters accumulated relatively higher concentrations than the species from tropical waters. The highest residue concentrations were found in Fraser's dolphins collected off Kii Peninsula, Japan (mean: 51 μg/g wet weight), reflecting serious PCB contamination in heavily industrialized areas. PCB input to the environment has still taken place due to the disposal of PCBs used in electrical equipment. This situation has led to the continuous contamination by PCBs in humans and wildlife. Elevated accumulation of PCBs was also previously reported in several cetacean species collected from Japanese coastal waters (Kannan *et al.* 1989a; Tanabe *et al.* 1988). Moreover, high concentrations were also observed in some open ocean species, such as northern right whale dolphin (30 μg/g wet weight) and Pacific white-sided dolphin (27 μg/g wet weight), which may be attributable to a wide migration range and distribution of these species (Carvadine 1995). Fras-

Harbor Porpoise Hokkaido, Japan 3 77 (70–90)		Dall's Porpoise Japan Sea 2 87 (86–89)		Northern Right Whale Dolphin Northern North Pacific 1 82		Pacific White-Sided Dolphin Northern North Pacific 1 76	
Conc. (ng/g)	TEQs (pg/g)	Conc. (ng/g)	TEQs (pg/g)	Conc. (ng/g)	TEQs (pg/g)	Conc. (ng/g)	TEQs (pg/g)
1.5 (0.4–3.5)	0.15 (0.04–0.35)	3.7 (3.6–3.8)	0.37 (0.36–0.38)	0.74	0.074	1.7	0.17
0.26 (0.20–0.34)	26 (20–34)	0.79 (0.78–0.80)	79 (78–80)	0.15	15	0.89	89
0.26 (0.11–0.44)	2.6 (1.1–4.4)	0.46 (0.43–0.48)	4.6 (4.3–4.8)	0.1	1.0	0.37	3.7
150 (97–230)	15 (9.7–23)	510 (420–600)	51 (42–60)	440	44	370	37
490 (260–840)	49 (26–84)	1,300 (1,000–1,600)	130 (100–160)	880	88	700	70
22 (11–31)	11 (5.5–16)	51 (37–64)	26 (19–32)	75	38	78	39
	100		290		190		240

Finless Porpoise Hong Kong 3 64 (29–87)		Spinner Dolphin Mindanao Sea, Philippines 2 66 (63–68)		Fraser's Dolphin Mindanao Sea, Philippines 2 66 (64–67)		Spinner Dolphin Bay of Bengal, India 3 66 (53–73)	
Conc. (ng/g)	TEQs (pg/g)	Conc. (ng/g)	TEQs (pg/g)	Conc. (ng/g)	TEQs (pg/g)	Conc. (ng/g)	TEQs (pg/g)
3.3 (0.56–6.0)	0.33 (0.06–0.6)	0.25 (0.20–0.29)	0.025 (0.02–0.03)	0.31 (0.21–0.41)	0.03 (0.02–0.04)	1.9 (0.8–2.9)	0.19 (0.08–0.29)
0.6 (0.27–0.92)	60 (27–92)	0.15 (0.13–0.16)	15 (13–16)	0.13 (0.08–0.17)	13 (8.0–17)	0.36 (0.15–0.58)	36 (15–58)
0.36 (0.28–0.43)	3.6 (2.8–4.3)	0.35 (0.28–0.41)	3.5 (2.8–4.1)	0.19 (0.11–0.27)	1.9 (1.1–2.7)	0.26 (0.14–0.32)	2.6 (1.4–3.2)
450 (140–750)	45 (14–75)	25 (24–26)	2.5 (2.4–2.6)	51 (31–70)	5.1 (3.1–7.0)	36 (31–42)	3.6 (3.1–4.2)
2,200 (510–3800)	220 (51–380)	80 (77–83)	8.0 (7.7–8.3)	150 (91–200)	15 (9.1–20)	99 (82–130)	9.9 (8.2–13)
130 (64–190)	65 (32–95)	12 (11–12)	6.0 (5.5–6.0)	19 (11–27)	9.5 (5.5–14)	21 (15–29)	16 (7.5–15)
	390		35		45		68

Data on hump-backed dolphin and finless porpoise from Hong Kong were cited from Minh *et al.* (1999).
Values in parentheses indicate the range.
* TEF values were cited from Van den Berg *et al.* (1998).

er's dolphins and spinner dolphins from the Philippines and India contained the lowest concentrations. In comparison with contamination status in other parts of the world (Table 1), average PCB concentrations in cetaceans from the North Pacific and Asian coastal waters (22 μg/g wet weight) were greater than those reported in killer whales, Risso's dolphins, Dall's porpoises, and harbor porpoises from coastal waters of British Columbia (Jarman *et al.* 1996), Atlantic spotted dolphins and pygmy sperm whales from the U.S. Atlantic coasts (Watanabe *et al.* 2000), and comparable to those found in harbor porpoises from the Black Sea (Tanabe *et al.* 1997) and common dolphins from Puck Bay, Poland (Falandysz *et al.* 1994). However, these levels were still significantly lower than those reported in the blubbers of striped dolphins, which were

victims of an epizootic in the western Mediterranean Sea during 1990–1992 and bottlenose dolphins and Risso's dolphins found dead along Italian coastal waters (Kannan *et al.* 1993; Corsolini *et al.* 1995) as well as in beluga whales from St. Lawrence River, Canada (Muir *et al.* 1996). Nevertheless, in some species from Japanese coastal waters, such as Fraser's dolphin collected off Kii Peninsula, PCB concentrations in the blubber approached the level associated with health risk of cetaceans (Wagemann and Muir 1984).

Isomer-Specific Accumulation

Figure 2 shows the percentage composition of PCB congeners in different cetacean species from the North Pacific and Asian coastal waters. Penta- and hexachlorobiphenyls were the most predominant congeners, accounting for about 70% of the total PCBs. In general, variations in PCB compositions were rather small among species examined. These results were somewhat different from those observed in diseased striped dolphins and stranded bottlenose and Risso's dolphins from the Mediterranean Sea, which showed the predominance of higher chlorinated biphenyls. In these species, induction of cytochrome P-450 monooxygenase due to the extremely elevated total PCB concentrations was suggested and consequently resulted in the biodegradation of lesser chlorinated congeners (Kannan *et al.* 1993; Corsolini *et al.* 1995).

Isomer-specific analysis of PCBs in the blubber of cetaceans revealed the presence of 61 individual congeners (Figure 3a, 3b). Hexachlorobiphenyl IUPAC No. 153 was the most prevalent congener, followed by IUPAC Nos. 138 and 180. In addition, IUPAC Nos. 52, 91/95, 99, 101, 118, 132, 144/149, 170, 177, 178, 187, and a U_7CB (heptachlorobiphenyl of unknown structure for which no standard was available) were also the major congeners in almost the species examined. It is interesting to note that the prevalence of lesser chlorinated congeners was found in cetaceans from cold and temperate waters in the northern regions, whereas species from tropical waters have higher chlorinated biphenyls as predominant congeners. As seen in Figure 3, tri-, tetra-, and pentachlorobiphenyls (e.g., IUPAC Nos. 47, 52, 84/90/92, 91/95, 99, 101, 118) in Dall's porpoises from Bering Sea and northeastern North Pacific, harbor porpoises from Hokkaido, Japan, and northern right whale dolphin from northern North Pacific accounted for relatively higher proportions than those of other species collected from the southern regions. The congener profiles in Figure 2 also support the trend observed in isomer-specific analysis.

In this context, behavior of individual PCB congeners in global terms should be considered. Lower chlorinated biphenyls, with high Henry's Law constants (HLCs), were shown to have negative flux by gas exchange across air-water interface in the Bering Sea and the North Pacific region (Iwata *et al.* 1993). As a result, semivolatile persistent OCs with higher HLCs tend to be transported to long distance toward the northern region. Lower chlorinated members (with higher HLCs) are more susceptible to atmospheric transport, preferentially deposited toward colder waters and accumulated in marine organisms in this region, including cetaceans. In the present study, results observed in cetaceans collected from Bering Sea and various locations in the North Pacific could be explained in the light of such a global redistribution phenomenon, which is mainly characterized by temperature dependent physicochemical properties of semivolatile persistent organic compounds.

On the other hand, results in PCB isomer–specific analysis of various kinds of cetaceans collected at different locations in the Asia-Pacific region may provide a plausible explanation regarding the implication of migration patterns of cetacean species to the contamination status in the locations where they were collected. These species were collected in the remote waters of the North Pacific Ocean and along coastal waters of Japan, Hong Kong, the Philippines, and India. According to the results in isomer-specific analysis (Figure 3a and 3b), the global fractionation phenomenon was clearly observed, particularly for the compositions of tri-, tetra-, and pentachlorobiphenyls. The decreasing trend of these compositions was observed in cetaceans collected from the northern to the southern areas of the Asia-Pacific region. The predominance of lower chlorobiphenyl congeners in cetaceans from cold and temperate waters is in accordance with the latitudinal fractionation, as discussed earlier. Thus, in this study, results of PCB accumulation in cetaceans collected from each location may reflect actual contamination status in that region, and the implication of migration of cetacean species seems to be minor.

Furthermore, it should be noted that some species, such as Dall's porpoise and common dolphin from the North Pacific Ocean, were collected during the period of 1985–1987, and therefore the temporal changes cannot be ruled out. However, according to our survey on temporal trend of organochlorines in cetaceans in the western North Pacific, there was no significant difference in total PCB residue levels as well as isomer and congener patterns in striped dolphins during the period of 1978–1986 (Longanathan *et al.* 1990). A recent temporal trend monitoring of organochlorine residues in minke whales collected from the North Pacific has revealed a steady-state of PCBs during 1987–1994 (Aono *et al.* 1997). In this context, it was also suggested that temporal change of PCBs in the remote waters was very slow and it could be attributable to the huge PCB load in the open ocean (Tanabe *et al.* 1988). In this study, although sampling time of cetaceans was different among locations, it is possible to draw some relevant interpretations regarding contamination status in view of the above findings, which showed the minor temporal changes in PCB residues and isomer patterns in cetaceans from the North Pacific Ocean.

Coplanar PCBs and Their Toxicological Impact

Concentrations of the most toxic non-*ortho* coplanar congeners, IUPAC Nos. 77, 126, and 169, as well as mono-*ortho* congeners IUPAC Nos. 105, 118, and 156 in various cetaceans species from North Pacific and Asian coastal waters are listed in Table 2. Mean concentrations (wet weight) of three non-*ortho* congeners ranged from 0.75 ng/g (in spinner dolphins from Philippines) to 6.6 ng/g (in Fraser's dolphins from off Kii Peninsula). In general, concentrations of IUPAC 77 were the highest among non-*ortho* congeners. Similar results were also observed in various aquatic mammals (Kannan *et al.* 1989a,

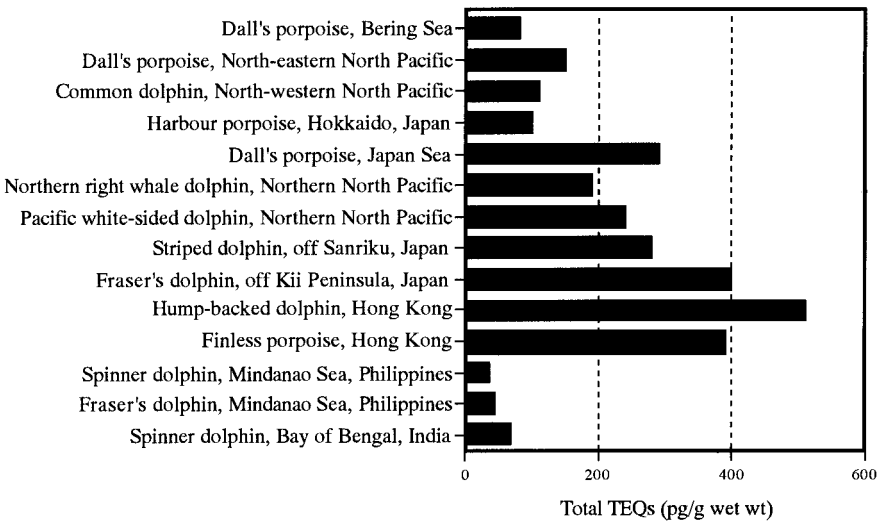

Fig. 4. 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin equivalents (TEQs) of non- and mono-*ortho* coplanar PCBs in the blubber of cetaceans from the North Pacific and Asian coastal waters

1993; Jarman *et al.* 1996; Muir *et al.* 1996; Tanabe *et al.* 1997; Storr-Hansen and Spliid 1993; Nakata *et al.* 1997, 1998), which may be attributable to its predominant existence in technical PCB preparations, three to four orders of magnitude greater than IUPACs 126 and 169, respectively (Kannan *et al.* 1993). Concentrations of mono-*ortho* congeners were about two to three orders of magnitude greater than those of non-*ortho* congeners (ranged from 120 to 2,900 ng/g wet weight) (Table 2).

Mammal-specific 2,3,7,8-TCDD toxic equivalency factors (TEFs) recently proposed by World Health Organization (WHO) (Van den Berg *et al.* 1998) were used to estimate the toxic equivalents (TEQs) of non- and mono-*ortho* PCB congeners detected in the blubber of cetaceans (Table 2). Mean concentrations of TEQs (wet weight) were considerably high in hump-backed dolphins (510 pg/g), finless porpoises (390 pg/g) from Hong Kong coastal waters, and Fraser's dolphins off Kii Peninsula (400 pg/g), while lower levels were observed from species in higher (Bering Sea and the North Pacific) and lower latitude regions (the Philippines and India). As shown in Figure 4, the TEQs in cetaceans from different locations indicated an increasing toxicological impact of coplanar PCBs in the mid-latitude region (Japan and Hong Kong), where industrial and human activities are very high and point sources of pollution are also conspicuous. Our earlier studies likewise showed elevated contamination by persistent OCs in various environmental compartments from Japan and Hong Kong (Kannan *et al.* 1989b, 1989c; Tanabe *et al.* 1987c, 1988; Minh *et al.* 1999).

In a comparison of estimated TEQ concentrations in cetaceans from other parts of the world, the highest levels found in this study (in cetaceans from Hong Kong and off Kii Peninsula) were higher than those estimated for the blubber of harbor porpoises from the Black Sea (Tanabe *et al.* 1997) and common porpoises from Puck Bay, Poland (Falandysz *et al.* 1994), and comparable to those of killer whales, Risso's dolphins, Dall's porpoises, and harbor porpoises from the coastal waters of British Columbia and California (Jarman *et al.* 1996). These levels are, however, apparently lower than those reported in striped dolphins affected by an epizootic in the western Mediterranean Sea and bottlenose dolphins and Risso's dolphins from Italian coastal waters (Kannan *et al.* 1993; Corsolini *et al.* 1995) as well as in beluga whales from the St. Lawrence River, Canada (Muir *et al.* 1996) (Table 1).

Among six coplanar congeners, mono-*ortho* IUPAC 118 or non-*ortho* IUPAC 126 has the greatest contribution to the total TEQs (Figure 5). Contribution of IUPAC 118 was prominent in species from high latitude oceans, such as the Bering Sea and the North Pacific, whereas non-*ortho* congener IUPAC 126 accounted for the highest contribution in cetaceans from lower latitude region, such as in the Philippines and India. In almost cetacean species, contributions of mono-*ortho* congeners to TEQs were predominant (Figure 5). Similar results were also reported in various cetaceans from other locations (Kannan *et al.* 1989a, 1993; Corsolini *et al.* 1995; Watanabe *et al.* 2000). Interestingly, increasing percentage of non-*ortho* coplanar congeners was found in cetacean species from high to low latitudes.

Mono-*ortho* coplanar congeners are metabolized by both 3-methylcholanthrene (MC, mainly cytochrome P450 1A subfamily—CYP1A) and phenobarbital (PB, mainly cytochrome P450 2B subfamily—CYP2B) type enzymes, whereas CYP1A is responsible for metabolism of non-*ortho* coplanar congeners (Boon *et al.* 1997). In addition, small cetaceans were characterized by relatively low MC-type activities and a deficient PB-type enzymes (Tanabe *et al.* 1988; Watanabe *et al.* 1989). Due to higher exposure of mono-*ortho* congeners and relatively weak induction of CYP2B enzymes, these congeners accumulate preferentially and contribute greater TEQs as compared to non-*ortho* congeners. However, the increasing pattern of non-*ortho* coplanar congeners in cetaceans from high to low latitude areas may be attributable to a decreasing biotransformation of non-*ortho* coplanar PCBs due to a lower potential for CYP1A induction. Alternatively, the behavior of these congeners in global terms can be another explanation for the observed pattern. Non-*ortho* coplanar congeners have relatively low values of Henry's Law constants (HLCs). For example, HLCs for IUPAC Nos. 77, 126, and 169 were estimated as 10.4, 8.29, and 6.60 Pa m^3/mol, respectively (Dunnivant and Eizerman 1992), which are in the range of those reported for DDT compounds (Iwata *et al.* 1993). Persistent semivolatile organic

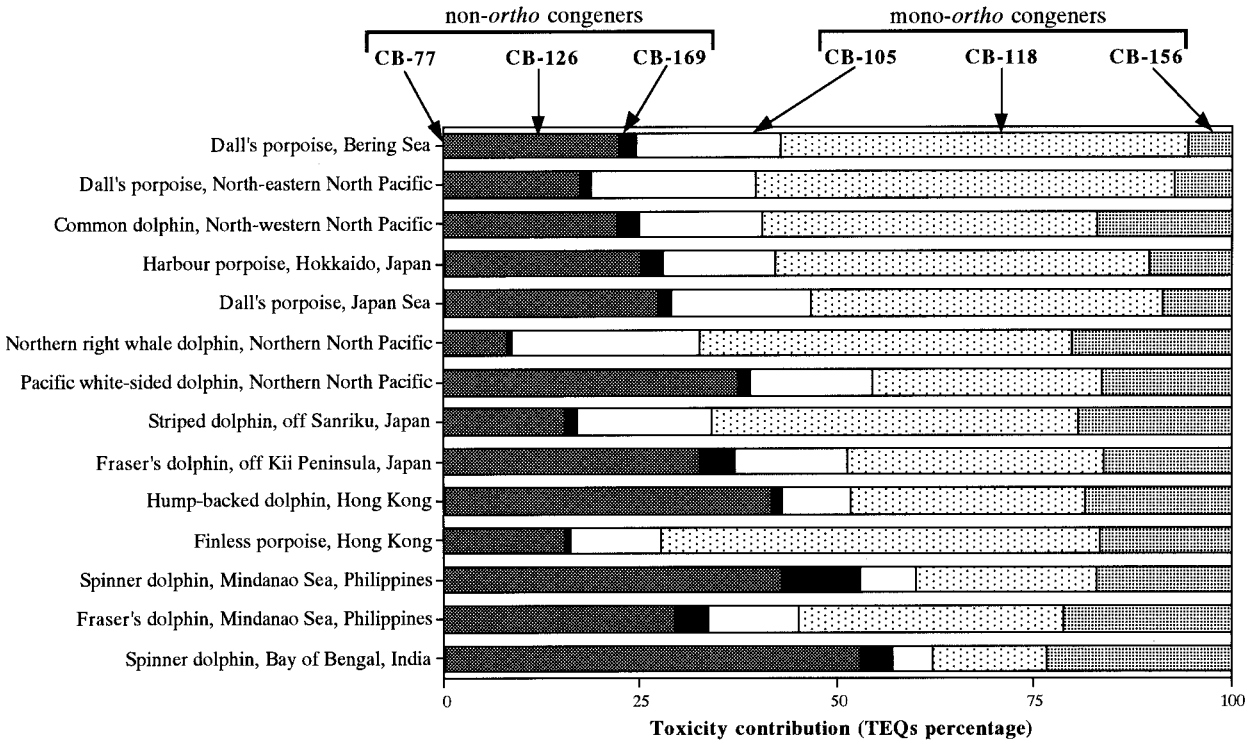

Fig. 5. Relative contribution to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin equivalents (TEQs) by non- and mono-*ortho* congeners in the blubber of cetaceans from the North Pacific and Asian coastal waters

compounds with low HLCs were characterized by low mobility to migrate around the globe (Iwata *et al.* 1993). In this case, less transportable nature of non-*ortho* PCBs through atmosphere might be a reason for the relative enrichment of these congeners in cetaceans from lower latitudes.

Considering these observations, it can be suggested that some cetaceans from the North Pacific and Asian coastal waters may have relatively high risk for the impacts of dioxin-like toxicity, because of the high bioaccumulation potential of toxic coplanar PCBs. Recent toxicological studies have suggested the biological effects of toxic coplanar PCBs in mammals. A total TEQ concentration of 209 pg/g (lipid weight) in the blubber may be associated with immunological dysfunctions in harbor seals (*Phoca vitulina*) (Ross *et al.* 1995). Residue level of 60 pg/g TEQs (wet weight) has been suggested to affect reproductive failure in mink (*Mustela vison*) (Tillitt *et al.* 1996). A recent investigation on exposure of beluga whale leukocytes has suggested that certain mixture of several most abundant PCB congeners found in the blubber of cetaceans might induce immunosuppresion (De Guise *et al.* 1998). Although no direct evidence is so far available on the definable relationship between toxic symptoms in cetaceans and persistent organchlorine residues, mean TEQ concentrations of toxic coplanar PCBs in the blubber of some odontoceti cetaceans measured in the present study, such as northern right whale dolphin (230 pg/g lipid weight) and Pacific white-sided dolphin (320 pg/g lipid weight) from northern North Pacific, Dall's porpoise from Japan Sea (330 pg/g lipid weight), striped dolphin off Sanriku (560 pg/g lipid weight) and Fraser's dolphin from off Kii Peninsula, Japan (570 pg/g lipid weight), hump-backed dolphin (1,100 pg/g lipid weight) and finless porpoise (610 pg/g lipid weight) from Hong Kong, exceeded the levels associated with immunosuppression in harbor seals as noted by Ross *et al.* (1995). Considering various suggestive indications of toxicity caused by organochlorines to marine mammals and the suspected link between mass mortalities and organochlorine residues, continued monitoring and ecotoxicological studies are necessary to understand the status of contamination as well as actual health effects of man-made chemicals, particularly PCBs and highly toxic coplanar congeners, on wild individuals and populations of cetaceans.

Acknowledgments. The authors wish to thank Prof. H. Ogi and K. Shimazaki (Faculty of Fisheries, Hokkaido University, Japan); Prof. T. Kasuya (Faculty of Bioresources, Mie University); Drs. K. Takagi and H. Tanaka (National Research Institute of Far Seas Fisheries, Japan); Dr. M. Amano (Ocean Research Institute, The University of Tokyo, Japan); Dr. Y. Fujise (Institute of Cetacean Research, Japan); Ms. P. Suarez (Silliman University, Dumaguete City, Negros Oriental, Philippines); and the staff of the Center of Advanced Study in Marine Biology, Annamalai University, India, for collection of cetacean samples. The collection of samples from Hong Kong was supported by grants from the Hong Kong Airport Authority and the Agriculture and Fisheries Department of the Hong Kong SAR Government. The assistance in collection of samples from stranded cetaceans of Dr. E. C. M. Parsons, Ms. I. Beasley, Ms. M. Torey, and several other individuals is acknowledged. We also wish to thank Dr. K. Kannan (Michigan State University) for critical reading of this manuscript. This study was supported by a Grant-in-Aid from the Scientific Research Programs of the Ministry of Education, Science and Culture of

Japan (Project nos. 12308030, 11878094, 09306021, and 09460086), and the 2nd Toyota High-Tech Research Grant Program.

References

Aguilar A, Borrell A (1994) Abnormally high polychlorinated biphenyl levels in striped dolphins (*Stenella coeruleoalba*) affected by the 1990–1992 Mediterranean epizootic. Sci Tot Environ 154: 237–247

Aono S, Tanabe S, Fujise Y, Kato H, Tatsukawa R (1997) Persistent organochlorines in minke whale (*Balaenoptera Acutorostrata*) and their prey species from the Antarctic and the North Pacific. Environ Pollut 98:81–89

Boon JP, van der Meer J, Allchin CR, Law RJ, Klungsoyr J, Leonards PEG, Spliid H, Storr-Hansen E, Mckenzie C, Wells DE (1997) Concentration-dependent changes of PCB patterns in fish-eating mammals: structural evidence for induction of cytochrome P450. Arch Environ Contam Toxicol 33:298–311

Carvadine M (1995) Whales, dolphins and porpoises. DK Publishing Inc., New York, NY, 256 pp

Colborn T, Smolen MJ (1996) Epidemiological analysis of persistent organochlorine contaminants in cetaceans. Rev Environ Contam Toxicol 146:91–172

Corsolini S, Focardi S, Kannan K, Tanabe S, Borrell A, Tatsukawa R (1995) Congener profile and toxicity assessment of polychlorinated biphenyls in dolphin, sharks and tuna collected from Italian coastal waters. Mar Environ Res 40:33–53

De Guise S, Martineau D, Béland P, Fournier M (1998) Effects of *in vitro* exposure of beluga whale leukocytes to selected organochlorines. J Toxicol Environ Health 55:479–493

Dunnivant FM, Eizerman AW (1992) Quantitative structure–property relationships for aqueous solubilities and Henry's Law constants of polychlorinated biphenyls. Environ Sci Technol 26:1567–1573

Falandysz J, Yamashita N, Tanabe S, Tatsukawa R, Rucinska L, Skóra K (1994). Congener-specific data on polychlorinated biphenyls in tissues of common porpoise from Puck Bay, Baltic Sea. Arch Environ Contam Toxicol 26:267–272

Giesy J, Kannan K (1998) Dioxin-like and non-dioxin-like toxic effects of polychlorinated biphenyls (PCBs): implications for risk assessment. Crit Rev Toxicol 28:511–569

Heide-Jorgensen MP, Harkonen T, Dietz R, Thompson P (1992) Reproductive of the 1988 European seal epizootic. Dis Aquat Organisms 13:37–62

Iwata H, Tanabe S, Sakai N, Tatsukawa R (1993) Distribution of persistent organochlorines in the oceanic air and surface seawater and the role of ocean on their global transport and fate. Environ Sci Technol 27:1080–1098

Iwata H, Tanabe S, Sakai N, Nishimura A, Tatsukawa R (1994) Geographical distribution of persistent organochlorines in air, water and sediments from Asia and Oceania and their implications for global redistribution from lower latitudes. Environ Pollut 85:15–33

Jarman WM, Norstrom RJ, Muir DCG, Rosenberg B, Simon M, Baird RW (1996) Levels of organochlorine compounds, including PCDDs and PCDFs, in the blubber of cetaceans from the west coast of North America. Mar Pollut Bull 32:426–436

Kannan N, Tanabe S, Ono M, Tatsukawa R (1989a). Critical evaluation of polychlorinated biphenyls toxicity in terrestrial and marine mammals: increasing impact of non-*ortho* and mono-*ortho* coplanar polychlorinated biphenyls from land to ocean. Arch Environ Contam Toxicol 18:850–857

Kannan N, Tanabe S, Tatsukawa R, Phillips DHJ (1989b) Persistency of highly toxic coplanar PCBs in aquatic ecosystem: uptake and release kinetics of coplanar PCBs in green-lipped mussels (*Perna viridis linnaeus*). Environ Pollut 56:65–76

Kannan N, Tanabe S, Okamoto T, Tatsukawa R, Phillips DJH (1989c) Polychlorinated biophenyls (PCBs) in sediments in Hong Kong: a congener-specific approach to the study of coplanar PCBs in aquatic ecosystem. Environ Pollut 62:223–235

Kannan K, Tanabe S, Borrell A, Aguilar A, Focardi S, Tatsukawa R (1993) Isomer-specific analysis and toxic evaluation of polychlorinated biphenyls in stripped dolphin affected by an epizootic in the western Mediterranean Sea. Arch Environ Toxicol 25:227–233

Kannan K, Senthikumar K, Loganathan BG, Takahashi S, Odell DK, Tanabe S (1997) Elevated levels of tributhyltin and its breakdown products in bottlenose dolphins (*Tursiops truncatus*) found stranded along the US Atlantic and Gulf coasts. Environ Sci Technol 31:296–301

Kannan K, Guruge KS, Thomas NJ, Tanabe S, Giesy JP (1998) Butyltin residues in southern sea otters (*Enhydra lutris nereis*) found dead along California coastal waters. Environ Sci Technol 32:1169–1175

Longanathan BG, Tanabe S, Tanaka H, Watanabe S, Miyazaki N, Amano M, Tatsukawa R (1990) Comparison of organochlorine residue levels in the striped dolphin from western North Pacific, 1978–79 and 1986. Mar Pollut Bull 21:435–439

Martineau D, Béland P, Desjardins C, Lagacé A (1987) Levels of organochlorine chemicals in tissues of beluga whales (*Delphinapterus leucas*) from the St. Lawrence estuary, Quebec, Canada. Arch Environ Contam Toxicol 16:137–147

Minh TB, Watanabe M, Nakata H, Tanabe S, Jefferson TA (1999) Contamination by persistent organochlorines in small cetaceans from Hong Kong coastal waters. Mar Pollut Bull 39:383–392

Muir DCG, Ford CA, Rosenberg B, Norstrom RJ, Simon M, Beland P (1996) Persistent organochlorines in beluga whales (*Delphinapterus leucas*) from the St. Lawrence River estuary—I. Concentrations and patterns of specific PCBs, chlorinated pesticides and polychlorinated dibenzo-*p*-dioxins and dibenzofurans. Environ Pollut 93:219–234

Nakata H, Tanabe S, Tatsukawa R, Amano M, Miyazaki N, Petrov EA (1997) Bioaccumulation profiles of polychlorinated biphenyls including coplanar congeners and possible toxicological implications in Baikal seal (*Phoca sibirica*). Environ Pollut 95:57–65

Nakata H, Tanabe S, Tatsukawa R, Koyama Y, Miyazaki N, Belikov S, Boltunov A (1998). Persistent organochlorine contaminants in ringed seals (*Phoca hispida*) from the Kara Sea, Russian Arctic. Environ Toxicol Chem 17:1745–1755

Ross PS, Swart RD, Reijnders PJH, Loveren HV, Vos JG, Osterhaus ADME (1995) Contaminant-related suppression of delayed-type hypersensitivity and antibody responses in harbour seals fed herring from the Baltic Sea. Environ Health Perspect 103:162–167

Safe SH (1994) Polychlorinated biphenyls (PCBs): environmental impact, biochemical and toxic responses, and implication for risk assessment. Crit Rev Toxicol 24:87–149

Storr-Hansen E, Spliid H (1993) Distribution pattern of polychlorinated biphenyl congeners in harbour seal (*Phoca vitulina*) tissues: statistical analysis. Arch Environ Toxicol 25:328–345

Swart RL de, Ross PS, Vedder EJ, Timmerman HH, Heisterkamp SH, van Loveren H, Vos JG, Reijnders PJH, Osterhaus ADME (1994) Impairment of immunological functions in harbour seals *Phoca vitulina* feeding on fish from polluted coastal waters. Ambio 23:155–289

Tanabe S (1988) PCB problem in the future: foresight from current knowledge. Environ Pollut 50:5–28

Tanabe S, Tatsukawa R (1992) Chemical modernization and vulnerability of cetaceans: increasing toxic threat of organochlorine contaminants. *In* Walker CH, Livingstone DR (eds) Persistent pollutants in marine ecosystem. Pergamon Press, New York, NY, pp 161–177

Tanabe S, Kannan N, Subramanian AN, Watanabe S, Tatsukawa R (1987a) Highly toxic coplanar PCBs: occurrence, source, persis-

tency and toxic implications to wildlife and humans. Environ Pollut 47:41–62

Tanabe S, Kannan N, Wakimoto T, Tatsukawa R (1987b) Method for the determination of three toxic non-*ortho* coplanar PCBs in environmental samples at part-per-trillion levels. Int J Environ Anal Chem 29:199–213

Tanabe S, Tatsukawa R, Phillips DJH (1987c) Mussel as bioindicators of PCBs pollution: a case study on uptake and release of PCB isomers and congeners in green-lipped mussels (*perna viridis*) in Hong Kong waters. Environ Pollut 47:41–62

Tanabe S, Watanabe S, Kan H, Tatsukawa R (1988) Capacity and mode of PCB metabolism in small cetaceans. Mar Mamm Sci 4:103–124

Tanabe S, Iwata H, Tatsukawa R (1994) Global contamination by persistent organochlorines and their ecotoxicological impact on marine mammals. Sci Total Environ 154:163–177

Tanabe S, Madhusree B, Öztürk AA, Tatsukawa R, Miyazaki N, Özdamar E, Orhan A, Samsun O, Öztürk B (1997) Isomer-specific analysis of polychlorinated biphenyls in harbour porpoise (*Phocoena phocoena*) from the Black Sea. Mar Pollut Bull 34:712–720

Tillitt DE, Gale RW, Meadows JC, Zajicek JL, Peterman PH, Heaton SN, Jones PD, Bursian SJ, Kubiak TJ, Giesy JP, Aulerich RJ (1996) Dietary exposure of mink to carp from Saginaw Bay. 3. Characterization of dietary exposure to planar halogenated hydrocarbons, dioxin equivalents, and biomagnification. Environ Sci Technol 30:283–291

Van den Berg M, Birnbaum L, Bosveld ATC, Brunström B, Cook P, Feeley M, Giesy JP, Hanberg A, Hasegawa R, Kennedy SW, Kubiak T, Larsen JC, Rolaf van Leeuwen FX, Djien Liem AK, Nolt C, Peterson R, Poellinger L, Safe S, Schrenl D, Tillitt D, Tysklind M, Younes M, Wærn F, Zacharewski T (1998) Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for human and wildlife. Environ Health Perspect 106:775–792

Wagemann R, Muir DCG (1984) Concentrations of heavy metals and organochlorines in marine mammals of northern waters: overview and evaluation. Canadian Technical Report of Fisheries and Aquatic Sciences No. 1279, Western Region, Department of Fisheries and Oceans, Canada

Wakimoto T, Tatsukawa R, Ogawa T (1971) Analytical method of PCBs. J Environ Pollut Cont 7:517–522

Watanabe S, Shimada T, Nakamura S, Nishiyama N, Yamashita N, Tanabe S, Tatsukawa R (1989) Specific profile of liver microsomal cytochrome P-450 in dolphin and whales. Mar Environ Res 27:51–65

Watanabe M, Kannan K, Takahashi A, Loganathan BG, Odell DK, Tanabe S, Giesy JP (2000) Polychlorinated biphenyls, organochlorine pesticides, *tris*(4-chlorophenyl)methane and *tris*(4-chlorophenyl)methanol in livers of small cetaceans stranded along Florida coastal waters, USA. Environ Toxicol Chem 19:1566–1574

Yamashita N, Tanabe S, Ludwid JP, Kurita H, Ludwid ME, Tatsukawa R (1993) Embryonic abnormalities and organochlorine contamination in double crested cormorants (*Phalacrocorax auritus*) and Caspian terns (*Hydroprogne caspia*) from the upper Great Lakes in 1988. Environ Pollut 79:163–173