Polybrominated Diphenyl Ethers and Organochlorines in Archived Northern Fur Seal Samples from the Pacific Coast of Japan, 1972—1998

NATSUKO KAJIWARA,[†] DAISUKE UENO,[†]
ATSUSHI TAKAHASHI,[†]
NORIHISA BABA,[‡] AND
SHINSUKE TANABE*,[†]

Center for Marine Environmental Studies (CMES), Ehime University, 2-5 Bunkyo-cho, Matsuyama 790-8577, Japan, and National Research Institute of Fisheries Science, 2-12-4 Fukuura, Kanazawa, Yokohama 236-8648, Japan

The present study clearly indicated possible prolonged and chronic marine pollution by polybrominated diphenyl ethers (PBDEs) unless the international regulatory measures are reinforced substantially. Fat tissues of female northern fur seals (Callorhinus ursinus), collected at 10 time periods between 1972 and 1998 from the Pacific coast of northern Japan, were analyzed for PBDEs and organochlorine compounds (OCs). PCBs and DDTs were the predominant contaminants in the fur seal samples. PBDEs were detected in all the samples analyzed, the values ranging from 0.33 to 100 ng/g lipid wt. with predominance of BDE-47. The lowest PBDE levels were in the fur seals collected in 1972, with the peak concentration around 1991—1994 and then decreased to about 50% in 1997—1998. Compositions of higher brominated congeners increased since 1972, while some lower brominated congeners decreased, implying a change in the pattern of use, particularly the increased use of highly brominated diphenyl ethers during 1972—1998. In the meantime, PCB compositions in fur seals showed no temporal variation, suggesting a continuous input of PCBs into the marine environment in significant quantities. As peak concentrations of PBDEs occurred later than OCs, it is essential to follow up the patterns of PBDEs pollution that may be of great concern in the future. To our knowledge, this is the first report on the contamination by PBDEs in marine mammals from the Asia—Pacific waters.

Introduction

Polybrominated diphenyl ethers (PBDEs) are one of the additive flame retardants widely used in plastics, textiles, and in electronic appliances including computers, televisions etc. (1), and some may contain up to 30% PBDEs by weight (2). PBDEs, similar in molecular structure to polychlorinated dibenzo-p-dioxins (PCDDs), furans (PCDFs), and biphenyls (PCBs), are of concern due to their persistence, bioaccumulation, and possible adverse effects in wildlife and humans

even in remote areas (3—5). Toxicological studies of limited PBDE congeners indicate that they are potential thyroid disruptors and developmental neurotoxicants (6, 7).

Growth in interest on PBDE flame retardants has been as exponential as their apparent increase in the environment over the past 20—25 yr in North America (4, 8, 9) and Europe (10, 11). However, there is still very little information on PBDE contamination and its temporal trend from other regions of the world, including the Asia—Pacific region. In Japan, the domestic demand on brominated flame retardants (BFRs) increased 3.4-fold from 20 000 t in 1986 to 67 250 t in 2000 (12). Recent studies have shown that PBDEs are distributed in several Japanese environmental media including sediments (13), fish (14, 15), and humans (16, 17). As for temporal studies, Choi et al. (16) compared PBDE residue levels in Japanese human adipose tissue collected in 1970 and 2000 and found that the concentrations increased 44 times during this period. Further studies to fill the gap between these two periods are needed. Also, Akutsu et al. (17) revealed that PBDE residues in the pooled Japanese human breast milk collected during the 1990s were apparently higher than those of 1970s. Since time—trend studies carried out so far in the Asia—Pacific region are limited to Japanese human samples, further studies are required in various environmental media and biota using a substantial number of sample and survey periods.

The present investigation attempts to comprehensively understand the temporal trend of contamination by PBDEs, emerging compounds, since 1972 in fat tissues of northern fur seals (Callorhinus ursinus) inhabiting and migrating in the North Pacific in comparison to classical organochlorine compounds (OCs). Previously, Tanabe et al. (18) reported PCBs, DDTs (dichlorodiphenyltrichloroethane and its metabolites), and HCHs (hexachlorocyclohexane isomers) residue levels in the same sample set collected between 1971 and 1988. The present study adds another decade of data on a variety of contaminants, including PBDEs.

Materials and Methods

Samples. Northern fur seal (C. ursinus) samples used in this study were collected off Sanriku, Japan, between 1972 and 1998 (Figure 1) and stored in the Environmental Specimen Bank for Global Monitoring (es-BANK) at Ehime University at −20 °C until analysis. Thirty-five mature females were employed for analysis (Table 1). In the animals collected prior to 1988, fat tissues around the mammary gland stored in formalin were used for chemical analysis, whereas frozen blubber samples were used for the others.

Chemical Analysis. Analysis of PBDEs was performed following the procedure described by Ueno et al. (5) with slight modification. Briefly, approximately 5 g of fat sample was ground with anhydrous sodium sulfate and extracted in a Soxhlet apparatus with a mixture of diethyl ether and hexane for 7—8 h. An aliquot of the extract, after adding 5 ng of internal standards ($^{13}C_{12}$-labeled BDE-3, BDE-15, BDE-28, BDE-47, BDE-99, BDE-153, BDE-154, BDE-183, and BDE-209), was added to a gel permeation chromatography column (GPC; Bio-Beads S-X3, Bio-Rad Laboratories, CA, 2 cm i.d. and 50 cm length) for lipid removal. The GPC fraction containing organohalogens was concentrated and passed through 1.5 g of activated silica gel S-1 (Wako Pure Chemical Industries Ltd., Japan) column with 5% dichloromethane in hexane for cleanup. $^{13}C_{12}$-labeled BDE-139 was added to the final solution prior to GC-MSD analysis. Quantification was
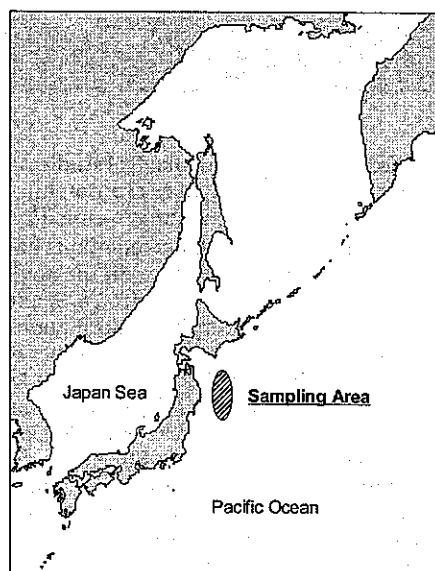
FIGURE 1. Sampling locations of northern fur seals.

performed using a GC (Agilent 6980N) equipped with MSD (Agilent 5973N) for mono- to hepta-BDEs and GC (Agilent 6980N) coupled with MSD (JEOL GCmate II) for deca-BDE, having an electron impact with selective ion monitoring mode (EI-SIM). GC columns used for quantification were DB-1 fused silica capillary (J&W Scientific Inc.) having 30 m × 0.25 mm i.d. × 0.25 μm film thickness for mono- to hepta-BDEs and 15 m × 0.25 mm i.d. × 0.1 μm film thickness for deca-BDE. Ten major congeners of PBDEs (BDE-3, BDE-15, BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, and BDE-209) were quantified in this study. All the congeners were quantified using the isotope dilution method to the corresponding $^{13}C_{12}$-labeled congener. Recovery of $^{13}C_{12}$-labeled BDE ranged between 60 and 120%.

OCs including PCBs, DDTs, HCHs, CHLs (chlordane related compounds), HCB (hexachlorobenzene), TCPMe [tris-(4-chlorophenyl)methane], and TCPMOH [tris(4-chlorophenyl)methanol] were analyzed following the methods described by Kajiwara et al. (19). Another aliquot of the extract was subjected to GPC for lipid removal. The GPC fraction containing OCs was concentrated and passed through an activated Florisil column for clean-up and fractionation. Quantification of PCBs and most of organochlorine pesticides was performed using a GC (Agilent 6980N) equipped with a microelectron capture detector (micro-ECD) and an auto-injection system (Agilent 7683 Series Injector). The GC column used for OCs analysis was a fused silica capillary (DB-1, 30 m × 0.25 mm i.d. × 0.25 μm film thickness, J&W Scientific Inc.). Identification and quantification of TCPMe and TCPMOH were performed using a GC-MSD (Agilent 5973N) in SIM mode equipped with an autoinjection system (Agilent 7683 series injector). The concentration of individual OCs was quantified from the peak area on the sample to that of the corresponding external standard. The PCB standard used for quantification was a mixture of 62 PCB isomers and congeners (BP-MS) obtained from Wellington Laboratories Inc., Ontario, Canada. Concentrations of individually resolved peaks of PCB isomers and congeners were summed to obtain total PCB concentrations.

Procedural blanks were analyzed simultaneously with every batch of five samples to check for interferences or contamination from solvents and glassware. Lipid contents were determined by measuring the total nonvolatile solvent extractable material on subsamples taken from the original extracts. The concentrations of organohalogens are expressed on a lipid weight basis unless otherwise specified.

TABLE 1. Concentrations of PBDEs and OCs (ng/g Lipid Weight) in Fat Tissues from Female Northern Fur Seals Collected off Sanriku, Japan, from 1972 to 1998[a]

year	n	age	BL (cm)	lipid (%)	PBDEs	PCBs	DDTs	CHLs	HCHs	HCB	TCPMe	TCPMOH
1972	3	20 (20–21)	128 (125–130)	67 (64–69)	0.34 (0.33–0.34)	8300 (7100–9400)	16000 (14000–18000)	750 (540–900)	1100 (1000–1100)	3.3 (2.8–4.3)	1.3 (1.1–1.4)	na
1976	3	21 (20–21)	134 (132–136)	22 (2.7–60)	4.3 (2.0–8.7)	16000 (9900–25000)	35000 (22000–57000)	2000 (1500–2700)	1200 (1100–1400)	0.80 (<0.2–2.4)	7.3 (1.8–17)	56 (8.2–89)
1980	2	21 (20,21)	135 (131–138)	75 (71–79)	8.5 (8.1–8.9)	2700 (2000–3400)	2800 (1800–3700)	590 (400–780)	550 (450–650)	2.3 (1.1–3.6)	0.51 (0.50–0.51)	8.7 (5.4–12)
1982	3	21 (20–22)	127 (120–136)	33 (23–38)	29 (22–37)	16000 (6400–24000)	38000 (8500–63000)	3100 (2000–4600)	1900 (1400–2200)	2.4 (<0.2–6.6)	6.5 (1.2–11)	58 (20–93)
1985	2	23 (22,23)	140 (132–148)	54 (48–60)	15 (12–18)	1800 (1200–2300)	1700 (840–2500)	700 (680–710)	960 (910–1000)	4.8 (3.5–6.1)	0.31 (0.12–0.50)	6.1 (3.4–8.7)
1988	2	20 (20,20)	135 (131–138)	76 (70–82)	47 (22–66)	3500 (2200–4700)	3100 (1400–4800)	1100 (650–1500)	540 (330–750)	1.2 (0.47–2.0)	0.68 (0.16–1.2)	13 (5.9–21)
1991	5	18 (17–20)	128 (123–134)	74 (64–80)	49 (35–66)	3400 (3200–3700)	1600 (1300–1800)	640 (430–880)	270 (130–460)	2.2 (0.84–4.1)	0.85 (0.61–1.1)	10 (4.7–19)
1994	5	15 (12–21)	130 (126–134)	75 (72–80)	53 (24–100)	2700 (1500–4300)	2800 (730–7900)	430 (210–1100)	380 (150–800)	1.1 (0.72–1.6)	na	na
1997	5	16 (11–22)	130 (125–135)	82 (77–100)	28 (21–40)	2600 (1900–3400)	1000 (700–1200)	420 (280–490)	160 (130–220)	2.2 (1.4–4.0)	0.63 (0.24–1.3)	6.8 (5.1–9.3)
1998	5	14 (12–17)	133 (121–140)	78 (72–88)	30 (22–38)	2200 (1500–3000)	1300 (620–2700)	570 (320–1100)	260 (190–330)	0.95 (0.39–2.1)	1.0 (0.52–1.5)	14 (6.4–26)

[a] Figures in parentheses indicate the range. n, number of samples. BL, body length. na, no data available.

For quality assurance and control, our laboratory participated in the Intercomparison Exercise for Persistent Organochlorine Contaminants in Marine Mammals Blubber, organized by the National Institute of Standards and Technology (Gaithersburg, MD) and the Marine Mammal Health and Stranding Response Program of the National Oceanic and Atmospheric Administration's National Marine Fisheries Service (Silver Spring, MD). Standard reference material (SRM 1945) was analyzed for selected PCB congeners and persistent OCs. Data from our laboratory were in good agreement with those for reference materials. The average of percentage deviation from the certified values was 13% (range: 0.5–20%) for organochlorine pesticides and 28% (range: 1.3–57%) for PCB congeners.

Results and Discussion

Temporal Trends of PBDEs. PBDE concentrations detected in the female northern fur seals are shown in Table 1. A total of eight congeners of di- to hepta-BDE were detected in fur seal fat. No BDE-3 (mono-BDE) and BDE-209 (deca-BDE) were found at the detection limit of the analysis, which were 0.01 and 0.5 ng/g on lipid wt., respectively. Concentrations of PBDEs ranged from a low value of 0.33 ng/g lipid wt. in 1972 to a high value of 100 ng/g lipid wt. in 1994 (Table 1). As a general trend, concentrations of PBDEs in fur seals were comparable to or higher than those of HCB, TCPMe, and TCPMOH and much lower than PCBs, DDTs, CHLs, and HCHs (Table 1). PBDE residue levels observed in the present study were apparently lower than those in marine mammals from Europe (20–24) and higher than those from Canadian Arctic (4). To our knowledge, this is the first comprehensive study revealing the accumulation of PBDEs in marine mammals from the Asia–Pacific waters.
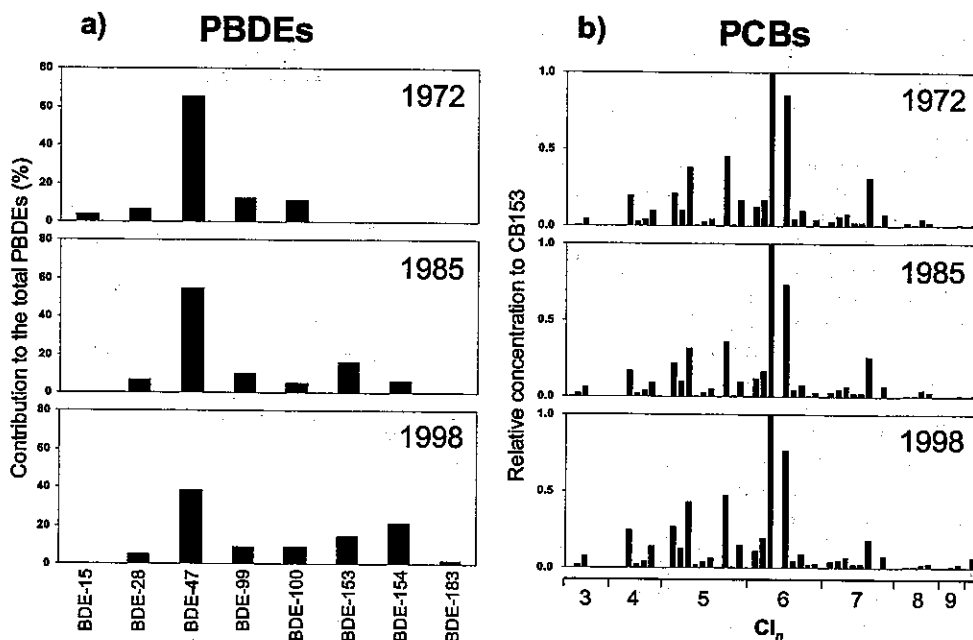
The lowest PBDE level was in the fur seals collected in 1972 (mean: 0.34 ng/g lipid wt.); the peak concentration was around 1991–1994. The average concentration of PBDEs increased to about 150 times between 1972 and 1994, and then levels decreased to about 50% in 1998 (Table 1 and Figure 2). Among the BFRs, there are mainly three commercial formulations that contain the diphenyl ether skeleton. In the order of increasing overall bromination, these formulations are named PentaBDE, OctaBDE, and DecaBDE. The reduction in PBDE levels observed in this study was probably a result of a voluntary phasing out the use of PentaBDE products by related Japanese industries in 1990 and the same in other countries affecting the Asia–Pacific waters. Since commercial OctaBDE usage was voluntarily restricted in Japan in 2000, the future trend should be studied. In the industrial regions of Europe, temporal trends for PBDEs suggest that while concentrations were increasing in human breast milk from the mid-1970s to late 1997, these levels appear to be leveling off or declining recently (25). This reduction in PBDE burdens in human milk is most probably the result of the regulatory measures in Europe to halt or regulate the use of Penta and OctaBDE products. On the other hand, temporal trends of PBDE concentration in herring gull eggs from the North American Great Lakes ecosystem (8) and ringed seals from the Canadian Arctic (4) showed an exponential increase, especially the lower brominated congener groups, PentaBDE. It has been suggested that the possible sources of these PentaBDE contaminations are the discarded PentaBDE impregnated materials such as polyurethane foam as well as direct vapor emission and wastewater from the related industries (2). The chronology of PBDE contamination of fur seals from northern Japan is different from that in the North American environment and rather similar to Europe.

Figure 3a shows the composition patterns of PBDEs detected in northern fur seals in 1972, 1985, and 1998. BDE-47 was the most abundant congener of the total PBDEs in
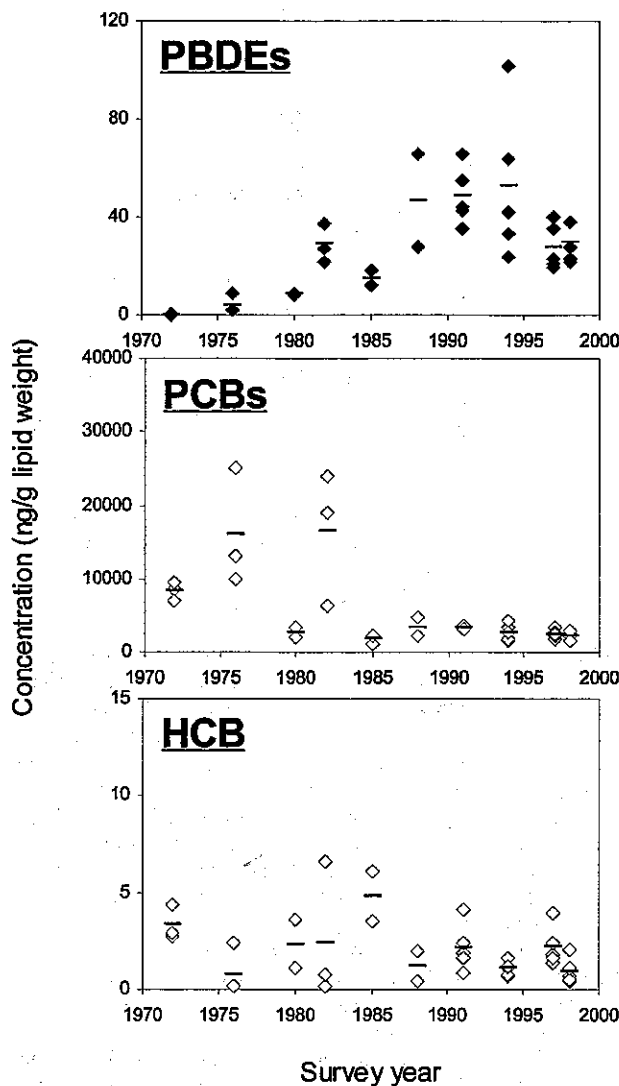
FIGURE 2. Temporal trend in concentration of PBDEs and OC residue in female northern fur seals collected from 1972 to 1998. Horizontal bars indicate mean values.

all the samples analyzed. Ratios of BDE-153, BDE-154, and BDE-183 to total PBDEs increased since 1972, while some lower brominated congeners decreased. Similar shift in PBDE congener profile between 1970 and 2000 was observed in Japanese human adipose tissue (16). This result implies an increase in demand particularly the highly brominated diphenyl ethers during 1972–1998. For example, the contribution of DecaBDE to the total domestic PBDE products in Japan changed from 67% in 1986 to 100% in 2000 (12). Although BDE-209, the primary component in DecaBDE, was not found in fur seal samples, photolytic debromination of this congener is reported to be a possible pathway for the formation of tetra- to nonaBDEs (26). Currently, debromination of BDE-209 to penta- to octa-BDEs has been reported in fish (27). Considering these facts, banning the lower BDE commercial mixtures and continuing the use of the DecaBDE formulation might have affected the BDE congener accumulation pattern to some extent in fur seals examined in the present study. Apart from DecaBDE, the two commercial BDE mixtures in use in Japan are the TetraBDE (which was estimated to be similar to the commercial PentaBDE in Europe and U.S.) and OctaBDE formulations (28). The Penta formulation consists primarily of BDE-47 and BDE-99, with lesser amounts of BDE-100 and BDE-153, and the Octa formulation consists of BDE-99, BDE-153, and BDE-154 as well as hepta- and octa-BDE congeners (29,30). The congener

a) PBDEs

1972 *1985* *1998*

Contribution to the total PBDEs (%)

BDE-15 BDE-28 BDE-47 BDE-99 BDE-100 BDE-153 BDE-154 BDE-183

b) PCBs

1972 *1985* *1998*

Relative concentration to CB153

3 4 5 6 7 8 9

Cl_n

FIGURE 3. Temporal variation of PBDEs and PCBs congener profiles in female northern fur seals collected in 1972, 1985, and 1998. Vertical bars represent (a) contribution of each congener to total PBDEs concentration and (b) concentrations of PCB congeners relative to the most abundant congener, CB-153, which was treated as 1.0.

profiles observed in this study, especially in the animals collected in 1998 having proportionately less BDE-47 and more BDE-154, were clearly different from those of marine mammals reported in Europe and the United States (*4, 23, 30, 31*). While they reported the PBDE accumulation pattern with a predominance of BDE-47 to more than 60% of the total, followed by BDE-99 and -100, the contribution by higher brominated congeners including BDE-153 and -154 was higher than PentaBDEs in this study. The type of commercial PBDE mixture used in these regions might elicit these differences in the profile.

PBDE levels in fur seals were compared with the annual consumption of commercial products. Figure 4a shows the annual consumption of three commercial PBDE formulations in Japan: TetraBDE, OctaBDE, and DecaBDE. Figure 4b shows temporal variations in levels of the sum of BDE-47, -99, and -100 in fur seals, as the tetra formulation consists primarily of these three congeners (*29*). On the other hand, Figure 4c shows those of the sum of BDE-153, -154, and -183, the constituents of the octa formulation (*32*), in fur seals. As shown in these figures, the levels of PBDEs in the TetraBDE mixture showed a decreasing trend in the fur seal bodies from the year 1990, whereas the constituents of the OctaBDE mixture started decreasing only a little later than 1990. It can be seen from these figures that the trends in fur seal bodies are not exactly following the usage pattern of the commercial PBDE formulations in Japan. Even though fur seal samples used in this study were collected from Japanese offshore waters, they migrate far north, up to the Bering Sea. Since Ueno et al. (*5*) recently reported a high potency of PBDEs to cause global pollution like PCBs through long-range atmospheric transport from regions where they were extensively used, some global input as well as local input should be considered. As mentioned previously, however, the congener profile observed in fur seals was not consistent with marine mammals from Europe and the U.S., implying that their contribution is not prominent. And hence, to elucidate this trend we need further information from all the areas including developing countries that may affect fur seals exposures to PBDEs.

Temporal Trends of OCs. OCs were detected in all the samples analyzed with predominance of PCBs and DDTs
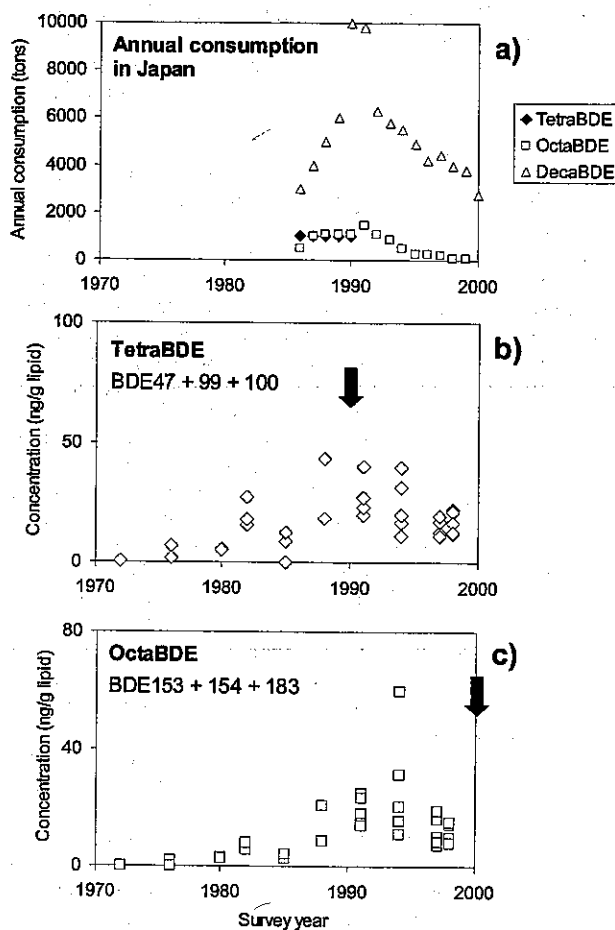
FIGURE 4. Comparison between the annual consumption of commercial PBDE products in Japan and the temporal trend in levels of certain PBDE congeners in northern fur seals. Arrows indicate the year when voluntary regulation started in Japan.

(Table 1). With the exception of HCB, OCs showed the highest levels in the 1970s to early 1980s and then decreased (Figure 2). This result implies the decrease in the usage and

environmental discharge of organochlorine contaminants into the North Pacific. The most obvious decline in the levels was noticed for DDTs (Table 1). The average concentration of DDTs in 1998 was only 3.7% of the level in 1976 with no apparent change in the composition of DDT and its metabolites throughout the survey. DDTs have a less transportable nature via atmosphere and water due to their low vapor pressure, low water solubility, and high particle affinity (33, 34). Even beyond these characteristics, the international restrictions had dramatic effects in DDT reduction in the environment.

The level of total PCBs in 1998 was about 14% of that in 1976. In all the time periods, congeners CB-153 and -138 dominated PCB profiles (Figure 3b). The congener specific analysis of PCBs indicated no difference in environmental input/ removal rates of individual congeners over a 26-yr period. It has been suggested that, although the production of PCBs was prohibited in Japan about 30 yr ago, this compound has been continuously released into the environment, mainly from old transformers and capacitors (35, 36). Consequently, PCBs are still in the environment, and the exposure will continue for a long time. Among the nations around Japan, the former Soviet Union produced technical PCB from the 1940s to the 1990s (37) in quantities greater than those produced in the United Kingdom, Japan, and Italy (38). Northern fur seals in this study might be reflecting the continuous input of PCBs mainly from Russia and Japan. The impact on the atmospheric transports from the major producers of PCBs such as the U.S. that has contributed almost 50% of the total global PCBs production (39) should also be considered. A low rate of decrease in the levels of PCBs indicates a possible prolonged exposure to these compounds that may be of concern in coming decades.

TCPMe and TCPMOH are the newly identified micro-contaminants. Although their pollution sources are still unclear, they have been considered the impurities in the technical pesticide preparations such as DDT (40) and dicofol (41), as well as synthetic high polymer and dye products (42). Regarding the toxicity of these compounds, recent in vivo and in vitro studies have shown their endocrine disrupting effects (43, 44). In the present study, the time–trend of TCPMe and TCPMOH residue patterns in fur seals were more or less the same with other major OCs with highest concentration in 1980, implying the culminated release of these contaminants into the environment around that time.

In contrast to other OCs, HCB residue levels in fur seals did not show any apparent decline (Figure 2). HCB has been used as a fungicide for crops and in certain industrial processes. Although HCB usage as a fungicide has been already banned worldwide, it is also generated as a byproduct during the production of several agro- and industrial chemicals. Furthermore, HCB has been released into the environment by waste incineration together with PCDDs and PCDFs (45, 46). Therefore, various sources of HCB might exist in the countries around the North Pacific.

Differences in the Temporal Trends between PBDEs and OCs. The pattern of temporal distribution of PBDEs in fur seals collected off Japan was apparently different from those of classical contaminants, OCs (Table 1 and Figure 2). Generally, OCs showed their highest levels in the 1970s to early 1980s and then decreased, whereas PBDEs were lower in the 1970s and were higher in the 1990s. Distribution of contaminants calculated as a percent of the sum of organohalogen compounds has changed during the time course studied. In 1972, DDTs was the predominant compound constituting 60% of the total organohalogen compounds. In 1998, the amount of DDTs decreased to 30%, and PCBs constituted the major part (50% of the total). The amount of PBDEs accounted for 0.001 and 0.7% in 1972 and 1998, respectively. Decrease in the levels of pesticides and com-

pounds originating from industrial usage confirms the positive effects of restrictions and prohibitions enforced on the usage of these compounds and other measures to minimize to pollution. However, as peak concentrations of PBDEs occurred later than OCs, we need further studies to follow-up the patterns of PBDEs pollution that may be of great concern in future.

It is noteworthy that the composition pattern of PBDEs showed a different shift from PCBs during the survey period (Figure 3). While PCB congener profiles in fur seals showed no temporal variation during the period between 1972 and 1998, the major PBDE congeners varied dramatically within the survey years. This result suggests that PBDEs is one of the contaminants with a high possibility of complex variations in the environment in the coming years. PBDE congener pattern seems to be unique depending on species, location, and year of sampling. Specific accumulation of PBDEs in various media should be studied in detail.

To our knowledge, this is the first-ever study carried out on PBDE levels in marine mammals from Asia–Pacific waters. Our investigation underlines the need for long-term monitoring of PBDEs pollution in this regions as well as OCs, including environmental and biotic samples. It is also imperative to find out potential sources of PBDEs and toxicological risk for marine mammals, the top predators of the ecosystem.

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