Polychlorinated Dibenzo- p -Dioxins, Dibenzofurans, and Polychlorinated Biphenyls in Human Tissues, Meat, Fish, and Wildlife Samples from India

ARTICLE *in* ENVIRONMENTAL SCIENCE AND TECHNOLOGY · SEPTEMBER 2001

Impact Factor: 5.33 · DOI: 10.1021/es010555+ · Source: PubMed

6 AUTHORS, INCLUDING:

Senthil Kumar Kurunthachalam
Sadara Chemical Company (Dow Chemical &…
114 PUBLICATIONS **3,205** CITATIONS
SEE PROFILE

Kurunthachalam Kannan
Wadsworth Center, NYS Department of Health
637 PUBLICATIONS **28,593** CITATIONS
SEE PROFILE

Shigeki Masunaga
Yokohama National University
205 PUBLICATIONS **3,348** CITATIONS
SEE PROFILE

Environ. Sci. Technol. **2001**, *35,* 3448−3455

Polychlorinated Dibenzo-*p*-Dioxins, Dibenzofurans, and Polychlorinated Biphenyls in Human Tissues, Meat, Fish, and Wildlife Samples from India

KURUNTHACHALAM SENTHIL KUMAR,*,† KURUNTHACHALAM KANNAN,‡ ODATHURAI N. PARAMASIVAN,§ VELLAKOVIL P. SHANMUGA SUNDARAM,|| JUNKO NAKANISHI,† AND SHIGEKI MASUNAGA†

Institute of Environmental Science and Technology, Yokohama National University, 79-7 Tokiwadai, Hodogaya-ku, Yokohama 240-8501 Japan, National Food Safety and Toxicology Center, Michigan State University, East Lansing, Michigan 48824, Kovai Medical Center and Hospitals, P.O. Box 3209, Avinashi Road, Coimbatore 641014, Tamil Nadu, India, and K. G. Hospital and Post Graduate Medical Institute, Arts College Road, Coimbatore 641018, Tamil Nadu, India

Concentrations of polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), and non- and mono-ortho-substituted polychlorinated biphenyls (dioxin-like PCBs) were measured in tissues of humans, fishes, chicken, lamb, goat, predatory birds, and Ganges River dolphins collected from various locations in India. PCDDs/DFs were found in most of the samples analyzed with the liver of spotted owlet containing the highest concentration of 3300 pg/g, fat wt. 2,3,7,8-Substituted PCDDs and PCDFs were found in human fat tissues at concentrations ranging from 170 to 1300 pg/g, fat wt. Concentrations of PCDDs were generally greater than those of PCDFs in human tissues, fishes, animal fat, and dolphin. Among fishes, meat, and wildlife samples analyzed, concentrations of PCDDs/DFs were found in the following order: country chicken < goat/lamb fat < fishes < river dolphins < predatory birds. Hepta-CDDs and OCDD were the major PCDD homologues found in humans, fishes, meat products, and dolphins. 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin equivalents of PCDDs/DFs were greater than those of PCBs in selected fish, dolphin, and human samples. To our knowledge, this is the first report of PCDDs and PCDFs in human tissues, fishes, meat, and wildlife collected from India.

Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs) are ubiquitous environmental contaminants. Several of the PCDD/DF congeners, particularly those substituted at 2,3,7,8-positions, are persistent and bioaccumulative. Since Baughman and Meselson (*1*) reported the occurrence of PCDDs/DFs in human tissues in the early 1970s, several studies have described the occurrence of these compounds in environmental media and biological tissues collected from various parts of the world (e.g., refs *2*−*5*). While various industrial practices have been attributed for the sources of PCDDs/DFs in the environment, stringent regulations to control their emissions in several developed countries have decreased exposures and thereby concentrations in humans and wildlife in recent years (*5*−*10*). Although studies have examined the occurrence of PCDDs/DFs in developed countries, little is known regarding the sources and exposure levels of humans and wildlife in India. Several chlorinated pesticides including 2,4-D and pentachlorophenol (PCP) are still being used in India (*11*, *12*). Effluents that contain PCDDs/DFs from pulp and papers mills that use chlorine bleaching are discharged onto agricultural land for the irrigation of crops in certain parts of India (*13*). Similarly, chlor-alkali plants employing graphite electrodes are located throughout India (*14*). Considering these, exposure of humans and wildlife to PCDDs/DFs in India is probable. Exposure to PCDDs/DFs is of concern because of the their toxicity, which include hormone-dependent cancers and reproductive effects in humans and wildlife (*3*, *15*−*18*). Nevertheless, prior to this study, no concentrations of PCDDs/DFs in humans and wildlife from India have been reported. In this study, fishes, meat products (lamb, chicken and goat), raptorial birds, Ganges River dolphin, and human tissues collected from various locations in India were analyzed for the presence of PCDDs, PCDFs, and PCBs that elicit the Ah receptor-mediated mechanism of toxic action (dioxin-like PCBs). 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD) equivalents (TEQs) were estimated using toxic equivalency factors (TEFs) reported by the World Health Organization (*18*).

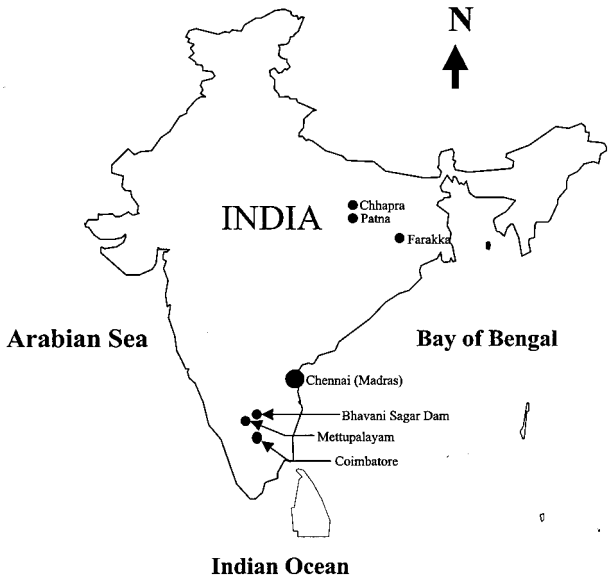

FIGURE 1. Map of India showing sampling locations.

Materials and Methods

Sample Collection. Fish samples [freshwater catfish (*Clarias* sp.), tilapia (*Tilapia nilotica*), and catla (*Catla catla*)] were collected in March 2000 by a hook and line in the Bhavani Sagar Water Reservoir (BSD) in Tamil Nadu, India (Figure 1). Two species of fishes caught [Indian sardine (*Sardinella*

* Corresponding author e-mail: senthil@ynu.ac.jp.
† Yokohama National University.
‡ Michigan State University.
§ Kovai Medical Center and Hospitals.
|| K. G. Hospital and Post Graduate Medical Institute.

10.1021/es010555+ CCC: $20.00

Published on Web 08/04/2001

TABLE 1. Concentrations (pg/g, Fat Weight) of PCDDs, PCDFs, and Dioxin-like PCBs in Fishes and Animal Fat from India

	fish[a]				Mettupalayam		
	Bhavani	Chennai	Patna	Farakka	chicken	lamb	goat
fat (%)	0.15	1.4	5.8	3.0	77	86	91
PCDDs							
2378-TCDD	<0.1	0.2	1.6	1.8	<0.1	0.2	<0.1
12378-PCDD	2.3	0.4	1.7	1.6	0.5	2.4	1.2
123478-HxCDD	0.6	0.5	3.4	1.2	0.8	0.8	<0.1
123678-HxCDD	0.4	0.8	9.4	4.0	0.8	4.2	3.0
123789-HxCDD	0.2	0.2	0.2	0.4	0.2	0.2	0.2
1234678-HpCDD	3.9	1.3	10	7.0	4.0	2.4	6.8
OCDD	26	6.1	56	24	5.0	2.4	7.8
∑PCDDs	33	9.5	82	40	11	13	19
PCDFs							
2378-TCDF	<0.1	<0.1	16	6.4	<0.1	1.4	0.2
12378-PCDF	<0.1	0.3	1.8	1.4	0.4	0.2	<0.1
23478-PCDF	0.3	0.4	20	4.0	<0.1	1.2	0.8
123478-HxCDF	0.3	0.2	3.0	1.0	0.8	1.0	1.0
123678-HxCDF	0.2	0.2	0.8	0.8	0.4	0.4	0.4
234678-HxCDF	0.4	0.3	0.8	0.6	0.7	0.4	<0.1
123789-HxCDF	<0.1	0.3	0.4	0.4	<0.1	<0.1	<0.1
1234678-HpCDF	1.7	0.5	2.0	1.2	0.3	0.6	1.2
1234789-HpCDF	0.6	0.4	0.4	0.2	0.2	<0.1	<0.1
OCDF	0.5	0.3	2.6	1.4	0.4	0.2	0.4
∑PCDFs	4.0	2.9	48	17	3.2	5.4	4.0
∑PCDDs/DFs	37	12	130	57	14	18	23
Dioxin-like PCBs							
344′5-TCB (81)[b]	<1	<1	340	38	<0.1	<10	<10
33′44′-TCB (77)[b]	96	18	500	540	<5.1	<10	<12
33′44′5-PCB (126)[b]	110	130	300	88	<3.7	<10	<6.8
33′44′55′-HxCB (169)[b]	<1	<1	74	22	<0.1	<10	<10
233′44′-PCB (105)[b]	550	440	9 800	7 000	26	56	98
2344′5-PCB (114)[b]	40	<1	340	240	<1	16	<1
23′44′5-PCB (118)[b]	1 500	1 300	1 000	20 000	58	72	<10
2′344′5-PCB (123)[b]	49	20	10	180	<1	20	<1
233′44′5-HxCB (156)[b]	170	160	1 800	2 600	6.2	76	56
233′44′5′-HxCB (157)[b]	41	32	640	600	4.0	22	11
23′44′55′-HxCB (167)[b]	1 500	71	1 200	1 200	16	<1	17
233′44′55′-HpCB (189)[b]	69	18	8.2	130	<1	11	20

[a] Pooled sample of several individuals; values below the detection limit were considered zero when calculating mean. [b] IUPAC Number.

longiceps) and golden anchovy (*Coillia dussumieri*)] from the Bay of Bengal in March 2000 were collected in a local market in Chennai. An edible portion of all the species from each location was pooled for analysis. Several species of fishes collected from the Ganges River in Patna in March 1994 (pool of *Mystus vittatus*, *Jhonius coiter*, *Labeo calbasu*, *Bagarius bagarius*, *Aoriichthys aor*, *L. bata*, and *Mastacembelus aramatus*) and Farakka in February 1997 (pool of *Notopterus chitala*, *N. notopterus*, *C. catla*, *Walago attu*, *Hilsa ilisha*, and *Puntius sarana*) were pooled. Animal fat samples from goat, lamb, and country chicken were collected from a local market in Mettupalayam. The sampling locations are shown in Figure 1.

Liver and blubber of Ganges River dolphins (*Platanista gangetica*) found drowned in fishing nets were collected from Chappra and Patna in 1994 and 1996. Bird samples were obtained from nomadic tribes in Coimbatore in March 2000. Bird species analyzed include spotted owlet (*Athene brama*) (2 females and 2 males weighing 60−61 g), a female osprey (*Pandion haliaetus*) weighing 144 g, a female prairie kite or Brahmany kite (*Haliastur indus*) weighing 210 g, a male black-winged kite (*Elanus caeruleus*) weighing 202 g, and an unidentified male eagle weighing 683 g. Upon collection, birds were sexed and weighed, and standard length was measured. Animals were frozen at 0 °C until dissected.

Human fat tissues (10 males and 11 females) were collected from volunteers with consent during biopsies performed at Kovai Medical Center and K. G. Hospital in Coimbatore. Tissue samples collected include 18 adipose fat, one thigh fat, one shoulder fat, and one breast fat. The age of the volunteers ranged from 20 to 69 yr. The patients were originally from the states of Tamil Nadu, Kerala, and Karnataka in southern India. Immediately after collection, the tissues were wrapped in aluminum foil and stored at −20 °C prior to analysis.

Analysis. Liver and muscle tissues of birds, Ganges River dolphin, and fishes were freeze-dried prior to analysis. Moisture content was determined from an aliquot of the samples. Details of the analytical procedures have been reported elsewhere (*19*−*22*). Tissues were extracted in a Soxhlet apparatus for 10 h using dichloromethane. Approximately 5−10 g of fat tissues of country chicken, goat, lamb, dolphin blubber, and human fat was ground with anhydrous sodium sulfate and extracted. After being extracted, the samples were concentrated using a Kuderna−Danish (K-D) concentrator, and the solvent was transferred to 10 mL of *n*-hexane. Fat content was determined gravimetrically from an aliquot of the extract. Seventeen 2,3,7,8-substituted ^{13}C-labeled tetra- through octa-CDD and CDF congeners and 12 dioxin-like PCBs (IUPAC Nos. 81, 77, 126, 169, 105, 114, 118, 123, 156, 157, 167, and 189) were spiked. Furthermore, aliquots were treated with sulfuric acid (approximately 7−10 times) in a separatory funnel. Then the hexane layer with PCDDs/DFs and PCBs was rinsed with hexane-washed water and dried by passing through anhydrous sodium sulfate in a glass funnel. The solution was

TABLE 2. Concentrations (pg/g Fat Wt) of PCDDs, PCDFs, and Dioxin-like PCBs in Bird and Ganges River Dolphin Tissues

	eagle	prairie kite	osprey	back-winged kite	spotted owlet		Ganges dolphin		
tissue	muscle	muscle	muscle	muscle	muscle[a]	liver ($n = 3$)	liver (C)[b]	liver (P)[c]	blubber (P)[d]
fat (%)	4.9	2.5	2.5	3.1	2.2	3.1 (2.1−4.0)	3.8	5.6	75 (74−76)
sex/length (cm)	M/57.3	F/33.1	F/34.5	M/31.7	2M, 2F/ 19.3−21.2	2M, 2F/ 19.3−21.2	F/84	M/133	1M, 1F/123−133
PCDDs									
2378-TCDD	2.3	23	<0.1	<0.1	21	60 (50−75)	2.4	8.6	1.8 (1.4−2.2)
12378-PCDD	5.6	74	64	41	<0.1	270 (230−340)	3.0	32	4.8 (3.2−6.4)
123478-HxCDD	<0.1	21	12	11	21	100 (90−100)	2.0	22	1.2 (1.0−1.6)
123678-HxCDD	16	120	76	45	120	840 (610−1 200)	3.6	26	6.4 (4.4−8.4)
123789-HxCDD	<0.1	3.8	8.3	<0.1	4.3	16 (13−18)	0.4	4.8	0.3 (0.2−0.4)
1234678-HpCDD	<0.1	<0.1	10	<0.1	56	260 (140−430)	5.0	46	6.2 (2.6−9.8)
OCDD	<0.1	<0.1	32	<0.1	51	260 (68−610)	34	84	7.6 (4.4−11)
∑PCDDs	24	240	200	97	270	1800 (1 300−2 700)	50	220	28 (15−35)
PCDFs									
2378-TCDF	2.1	27	64	12	12	50 (36−75)	6.0	24	9.2 (7−13)
12378-PCDF	1.2	21	<0.1	<0.1	14	24 (0−52)	0.8	20	2.8 (2.2−3.4)
23478-PCDF	9.0	49	40	27	56	360 (260−480)	4.2	24	4.8 (3.8−5.6)
123478-HxCDF	3.6	15	<0.1	7.6	21	190 (91−330)	1.4	18	1.0 (0.8−1.2)
123678-HxCDF	<0.1	14	<0.1	7.8	17	87 (64−99)	1.2	20	1.4 (0.8−2.0)
234678-HxCDF	<0.1	<0.1	11	<0.1	15	89 (82−110)	1.0	26	1.2 (0.6−1.8)
123789-HxCDF	0.1	0.5	0.8	1.0	<0.1	8.6 (6.9−12)	1.4	20	0.2 (0.2)
1234678-HpCDF	<0.1	<0.1	6.0	<0.1	8.7	33 (23−41)	2.6	20	1.2 (0.6−1.6)
1234789-HpCDF	<0.1	<0.1	5.5	3.6	4.4	7 (4.6−9.5)	1.0	8.0	0.1 (0.1−0.2)
OCDF	2.9	0.0	22	<0.1	9.2	9.1 (5.9−11)	4.4	15	0.8 (0.6−0.8)
∑PCDFs	19	130	150	59	160	860 (620−1 000)	24	200	22 (11−19)
∑PCDDs/DFs	43	370	350	160	430	2 600 (2 300−3 300)	74	420	50 (34−68)
Dioxin-like PCBs									
344′5-TCB (81)[e]	69	1.2	12	30	20	710 (620−780)	24	140	56 (26−88)
33′44′-TCB (77)[e]	110	97	450	650	82	1 500 (1 200−1 700)	82	480	180 (72−280)
33′44′5-PCB (126)[e]	120	490	570	850	420	4 700 (2 800−7 900)	96	320	110 (80−150)
33′44′55′-HxCB (169)[e]	14	230	64	530	200	640 (250−1 000)	16	80	24 (24−26)
233′44′-PCB (105)[e]	5 500	5 800	12 000	1 700	5 000	14 000 (1 700−3 7 000)	1 500	32 000	12 000 (5 000−20 000)
2344′5-PCB (114)[e]	INT[f]	1 300	1 600	260	420	1 700 (460−4 200)	140	2 200	1 000 (620−1 500)
23′44′5-PCB (118)[e]	650	18 000	37 000	8 000	13 000	17 000 (13 000−26 000)	5 000	70 000	18 000 (580−36 000)
2′344′5-PCB (123)[e]	INT[f]	1 100	1 200	250	210	81 (9.3−220)	180	2 400	300 (22−560)
233′44′5-HxCB (156)[e]	2 300	4 400	10 000	1 100	2 700	8 700 (6 800−1 0000)	780	8800	3 700 (2 400−5 000)
233′44′5′-HxCB (157)[e]	570	1 100	2 300	510	1 500	1 400 (990−2 000)	200	2 200	900 (570−1 200)
23′44′55′-HxCB (167)[e]	700	3 100	6 000	330	1 200	4 200 (1 800−6 600)	380	4 200	1 800 (1 200−2 400)
233′44′55′-HpCB (189)[e]	19	750	680	910	660	1 200 (710−2 300)	30	660	220 (170−270)

[a] Pooled samples; values in parentheses indicate the range. [b] Liver of dolphin from Chappra collected in January 1994. [c] Liver of dolphin from Patna collected in November 1996. [d] Blubber samples from Patna were taken from dolphins stranded in November 1994 (male) and 1996 (female). [e] IUPAC Number. [f] INT, possible interference.

concentrated to 2 mL and sequentially subjected to silica gel, alumina, and silica gel-impregnated activated carbon column chromatography. Extracts were passed through a silica gel-packed glass column (Wakogel, silica gel 60; 2 g) and eluted with 130 mL of hexane. The hexane extract was K-D concentrated and passed through alumina column (Merck-Alumina oxide, activity grade 1; 5 g) and eluted with 30 mL of 2% dichloromethane as a first fraction, which contained multi-ortho-substituted PCBs. The second fraction eluted with 30 mL of 50% dichloromethane in hexane, containing non- and mono-ortho-PCBs and PCDDs/DFs, was K-D concentrated and passed through silica gel-impregnated activated carbon column (0.5 g). The first fraction eluted with 25% dichloromethane in hexane contained mono- and di-ortho-PCBs. The second fraction eluted with 250 mL of toluene containing PCDDs/DFs was concentrated and analyzed using a high-resolution gas chromatograph interfaced with a high-resolution mass spectrometer (HRGC−HRMS).

Identification and Quantification. Identification and quantification of 2,3,7,8-substituted congeners of PCDDs/DFs and dioxin-like PCBs (non- and mono-ortho-substituted congeners) was performed by use of a Hewlett-Packard 6890 series HRGC interfaced with a Micromass Autospec−Ultima HRMS. The HRMS was operated in an electron impact (EI) and selected ion monitoring (SIM) mode at a resolution $R > 10\,000$ (10% valley). Separation was achieved using DB-5 (J&W Scientific; 0.25 mm i.d. × 60 m length) and DB-17 capillary (J&W Scientific; 0.25 mm i.d. × 60 m length) columns. The column oven temperature was programmed from an initial temperature of 160 °C to a final temperature of 310 °C (total running time 60 min). Recoveries of 17 2,3,7,8-substituted ^{13}C-labeled PCDDs/DFs were from 57 to 95% (mean: 78%). The concentrations are expressed as picogram per gram on a fat weight basis. Detection limits varied from 0.1 to 10 pg/g, fat wt, depending on the congeners and potential interferences.

Results and Discussion

Concentrations in Fish and Meat. Concentrations of 2,3,7,8-substituted PCDDs and PCDFs in fishes varied from 9.5 to 82 and from 2.9 to 48 pg/g, on a fat weight basis, respectively (Table 1). Fishes from the Ganges River in Patna contained the highest concentration of total PCDDs/DFs (130 pg/g, fat wt) whereas those collected from the Bay of Bengal in Chennai contained the lowest concentration (12 pg/g, fat wt). Concentrations of PCDDs were 2−8-fold greater than those of PCDFs in fishes (Figure 6 in Supporting Information). 1,2,3,4,6,7,8-HpCDD and OCDD were the predominant congeners accounting for 77−100% of the total PCDD concentrations in fishes. In addition to PCDD congeners, 2,3,7,8-TCDF and 2,3,4,7,8-PCDF were also found in fishes

from the Ganges River (Figure 7 in Supporting Information). The pattern of PCDDs/DFs in fishes from the Bhavani water reservoir was similar to those reported for pentachlorophenol (*23*). Relatively great concentrations of PCDFs in fishes from the Ganges River suggest the presence of PCDF sources. Particularly, predominance of 2378-TeCDF, 23478-PeCDF, and HxCDD in fishes from the Ganges River suggests that the sources originated from chlorine bleaching of pulp and paper mills.

The sum of concentrations of 12 dioxin-like PCB congeners in fishes ranged from 2200 to 32 000 pg/g, fat wt (Table 1). On a wet weight basis, the concentrations of 12 PCB congeners in fish ranged from 24 to 260 pg/g. These concentrations are similar to or less than those reported earlier for fish from Patna (*24*, *25*). Among dioxin-like PCBs, congener 118 accounted for the major proportion of the total concentrations followed in decreasing order by congeners 105, 156, 167, and 157 (Figure 8 in Supporting Information). Non-ortho-coplanar PCBs were found in fishes at 2−8% of the total dioxin-like PCB concentrations. In general, studies have shown that the concentration of PCBs in Indian environment is much less than that in developed countries such as the United States and Japan (*26*).

Concentrations of PCDDs and PCDFs in animal origin foods (country chicken, lamb, and goat) ranged from 11 to 19 and from 3.2 to 5.4 pg/g, fat wt, respectively (Table 1). The concentrations of PCDDs/DFs in meat products were, on average, 2−5-fold less than those found in fishes. Similar to that found for fishes, the concentrations of PCDDs were greater than those of PCDFs. Hepta- and octa-CDDs were the predominant congeners in the fat of chicken and goat accounting for 50% of the total PCDD concentrations (Figure 7 in Supporting Information). In the lamb fat, several PCDD and PCDF congeners were found. The presence of a range of PCDD/DF congeners at low concentrations in meat products suggests exposure to generic sources derived from atmospheric deposition. In general, concentrations of PCDDs and PCDFs in animal origin foods in India were less than those reported from the United States and Japan (*27*, *28*). The sum of concentrations of 12 dioxin-like PCBs in meat products ranged from 110 to 270 pg/g, fat wt. Among dioxin-like PCBs, congeners 105, 118, and 156 were predominant in meat products (Figure 8 in Supporting Information). These concentrations were less than those reported for developed countries (*27*, *28*). An earlier study has reported the occurrence of relatively less concentration of PCBs in meat products (3.6 ng/g, wet wt) from India (*29*).

Concentrations in Dolphins and Birds. The liver of Ganges River dolphins contained approximately 3-fold higher concentrations of PCDD/DFs than those of fishes from the Ganges River (Table 2). Concentrations of total PCDDs/DFs in the liver and blubber of dolphins were 74−420 and 34−68 pg/g, fat wt, respectively. The liver of dolphin from Patna contained 6 times higher concentrations of PCDDs/DFs than that from Chappra. Lipid-normalized concentrations of PCDDs/DFs in livers were 2−6-fold greater than that in the blubber. Concentrations of PCDDs were similar to those of PCDFs in dolphins from Patna (Figure 6 in Supporting Information). However, the concentrations of PCDDs were 2-fold greater than those of PCDFs in livers of dolphins from Chappra. Interestingly, all 17 2,3,7,8-substituted congeners were present in both liver and blubber of dolphins. Although hepta- and octa-CDDs were the predominant congeners in dolphins, 12378-PCDD, 123678-HxCDD, 2378-TCDF, 12378-PCDF, 23478-PCDF, 123789-HxCDF, 1234678-HpCDF, and OCDF were also found at considerable concentrations (Table 2 and Figure 7 in Supporting Information). The presence of a variety of congeners suggests multiple sources including waste uncontrolled open incineration, PCP, and sewage disposal (*30*). The presence of notable concentrations of 2378-TeCDF suggests pulp mill-related sources while OCDF and HpCDF are indicative of sources originating from chlor-alkali processes (*6*). Several pulp mills, textiles mills, fertilizer and pesticide industries, and chlor-alkali plants are located along the Ganges River in India (*14*).

TABLE 3. Mean (Range) Concentrations of PCDDs, PCDFs, and Dioxin-like PCBs (pg/g, Fat Wt) in Human Fat from Southern India

sex fat (%)	males ($n = 10$) 77 (72−82)	females ($n = 11$) 75 (62−85)
	PCDDs	
2378-TCDD	1.6 (0.6−2.8)	2.0 (0.6−5.8)
12378-PCDD	4.8 (1.6−9.4)	5.2 (1.6−12)
123478-HxCDD	2.4 (1.2−6.2)	4.0 (1.2−14)
123678-HxCDD	20 (8.2−48)	22 (9.0−38)
123789-HxCDD	1.0 (0.4−1.6)	1.8 (0.8−2.8)
1234678-HpCDD	74 (30−240)	110 (40−220)
OCDD	340 (120−920)	440 (170−960)
∑PCDDs	440 (160−1 200)	590 (220−1 300)
	PCDFs	
2378-TCDF	1.0 (0.1−0.9)	0.8 (0.4−1.4)
12378-PCDF	0.6 (<0.1−0.9)	0.3 (<0.1−0.9)
23478-PCDF	9.8 (1.3−9.5)	3.0 (<0.1−4.5)
123478-HxCDF	3.8 (0.8−3.5)	1.6 (0.8−3.4)
123678-HxCDF	3.4 (0.8−3.4)	1.4 (0.9−2.2)
234678-HxCDF	1.6 (0.4−1.3)	0.8 (0.4−1.3)
123789-HxCDF	0.2 (0.1)	0.1 (0.1−0.2)
1234678-HpCDF	12 (2−18)	4.7 (2−16)
1234789-HpCDF	0.2 (<0.1−0.2)	0.1 (<0.1−0.3)
OCDF	1.2 (0.2−3.6)	1.2 (0.4−3.6)
∑PCDFs	33 (11−80)	26 (9.6−64)
∑PCDDs/PCDFs	480 (170−1 300)	620 (230−1 300)
	Dioxin-like PCBs	
344′5-TCB (81)[a]	14 (<0.1−60)	18 (<0.1−88)
33′44′-TCB (77)[a]	24 (6.0−86)	56 (13−160)
33′44′5-PCB (126)[a]	120 (24−360)	130 (42−380)
33′44′55′-HxCB (169)[a]	30 (4.0−120)	28 (4.6−54)
233′44′-PCB (105)[a]	2 600 (500−17 000)	1 500 (300−5 600)
2344′5-PCB (114)[a]	480 (60−3000)	220 (44−800)
23′44′5-PCB (118)[a]	3 000 (1 400−4 600)	4 000 (82−24 000)
2′344′5-PCB (123)[a]	18 (<0.1−48)	17 (<0.1−66)
233′44′5-HxCB (156)[a]	1 400 (240−5 000)	1200 (130−6 200)
233′44′5′-HxCB (157)[a]	620 (64−4 200)	260 (36−1 100)
23′44′55′-HxCB (167)[a]	320 (74−1 200)	400 (50−2 200)
233′44′55′-HpCB (189)[a]	150 (15−880)	40 (<0.1−110)

[a] IUPAC Number.

Mono-ortho-PCB congeners (105, 118, 156, and 167) accounted for greater than 95% of the concentrations of dioxin-like PCBs in dolphins (Figure 8 in Supporting Information). Livers of dolphins from Patna contained 6 times greater PCB concentrations than that from Chappra. Non-ortho-PCBs accounted for 0.8−2.5% of the dioxin-like PCB concentrations in dolphins. Variations in the concentrations of PCDDs/DFs and PCBs between two individuals could be explained by the gender difference. Tissues of male dolphin contained higher concentrations than those of females. The transfer of organochlorine compounds via lactation is an explanation for the lower concentrations in females (*24*).

Concentrations of PCDDs/DFs in the muscle of spotted owlet were the highest (430 pg/g, fat wt) followed in decreasing order by prairie kite (360 pg/g, fat wt), osprey (350 pg/g, fat wt), black-winged kite (160 pg/g, fat wt), and eagle (43 pg/g fat wt) (Table 2). Concentrations of PCDDs were approximately 1.5 to 2-fold greater than those of PCDFs in birds (Figure 6 in Supporting Information). Concentrations of PCDDs/DFs in spotted owlet liver were 6 times higher than that in the breast muscle. Mean PCDD and PCDF concentrations in Indian birds were less than those reported in the tissues of fish-eating birds from Japan, the United States, Canada, Switzerland, and the Baltic Sea (*31*−*33*).

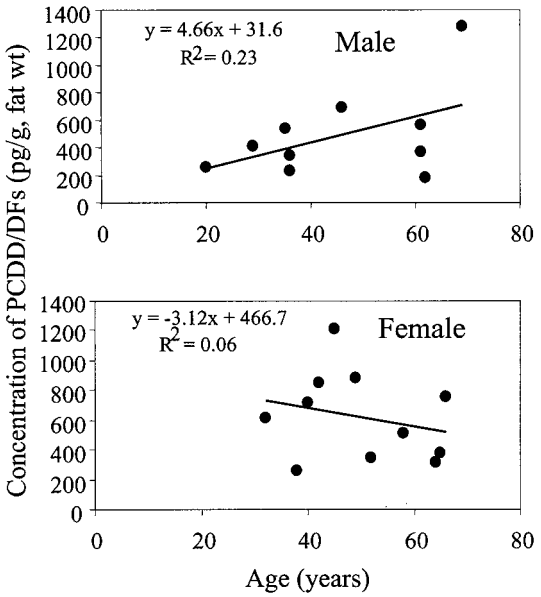

FIGURE 2. Relationship between concentrations of PCDD/DFs and age in Indian adipose fat.

Similarly, the concentrations of dioxin-like PCBs in Indian birds were lower than those reported for birds from Japan, the Baltic Sea, Canada, the United States (*31*−*35*) and higher than those reported from China (*36*) and Switzerland (*37*). Total PCB concentration of up to 1000 ng/g, wet wt, was reported in spotted owlets collected from India (*38*, *39*).

The distribution pattern of PCDD/DF congeners in five species of birds varied considerably. 2378-TCDD was present at considerable concentrations in spotted owlet and prairie kite (Table 2 and Figure 7 in Supporting Information). 123678-HxCDD and 23478-PeCDF were the predominant congeners in birds. In addition, 12378-PCDD, 123478-HxCDD (except eagle), 2378-TCDF, and 23478-PCDF were also found in bird tissues at noticeable concentrations (Table 2 and Figure 7 in Supporting Information). Notably, hepta-CDD and OCDD, which were predominant in fishes and dolphin, were either not detected or were present at low concentrations in birds. PCDD/DF congener patterns in muscle and liver of spotted owlet suggested an enrichment of 12378-PCDD and 234678-HxCDF in liver while these congeners were not found in muscle. PCB congeners 105, 118, 156, and 167 were the major dioxin-like PCB congeners found in birds (Figure 8 in Supporting Information), which is similar to that reported earlier (*38*, *39*).

Concentrations in Human Tissues. Concentrations of PCDDs/DFs in 18 adipose fat, one breast fat, one thigh fat, and one shoulder fat of humans from southern India ranged from 170 to 1300 pg/g, fat wt (mean: 540 pg/g, fat wt) (Table 3). Concentrations of PCDDs (520 pg/g) were, on average, 17-fold greater than those of PCDFs (30 pg/g) in human tissues (Figure 6 in Supporting Information). Almost all 17 2,3,7,8-substituted PCDDs/DFs were found in human fat tissues except 12378-PCDF and 1234789-HpCDF in certain individuals. Among PCDDs, 1234678-HpCDD and OCDD were the most abundant congeners in humans (Figure 7 in Supporting Information), which is similar to that observed in fish, meat, and dolphins. OCDD has been commonly found in human tissues from most countries (*19*, *40*−*46*). Among dioxin-like PCBs, congener 126 is the most prevalent among the non-ortho-PCBs in most human fat samples except two samples, which contained congener 77 at greater concentrations (Table 3 and Figure 8 in Supporting Information).

The mean concentration of ∑PCDD/DFs in males was 480 pg/g, fat wt ($n = 10$). A slightly higher concentration has been observed for females (620 pg/g), although this was not statistically significant ($p > 0.05$). The number of samples ($n = 21$; 10 males and 11 females) analyzed is small to examine age and gender-specific differences in concentrations of PCDDs/DFs. Nevertheless, the available data suggested an increase in concentrations with age for males while a constant or decline in concentrations with age for females (Figure 2), which is similar to that observed in several other countries (*40*, *47*). While some studies have reported gender differences in PCDD/DF concentrations, a few other studies have showed no such differences in PCDD/DF concentrations between males and females (*47*−*49*). Concentrations of PCDDs/DFs in human tissues are influenced by a number of factors

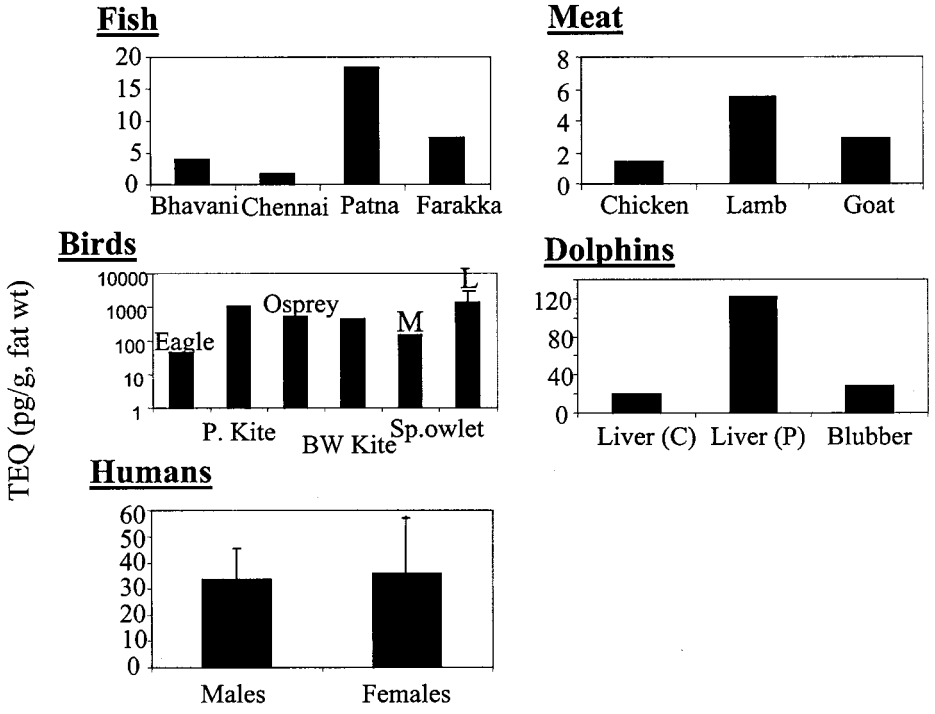

FIGURE 3. Toxic equivalents (TEQs; pg/g, fat wt) in fish, meat, dolphin, birds, and human adipose fat from India. M, muscle; L, liver.

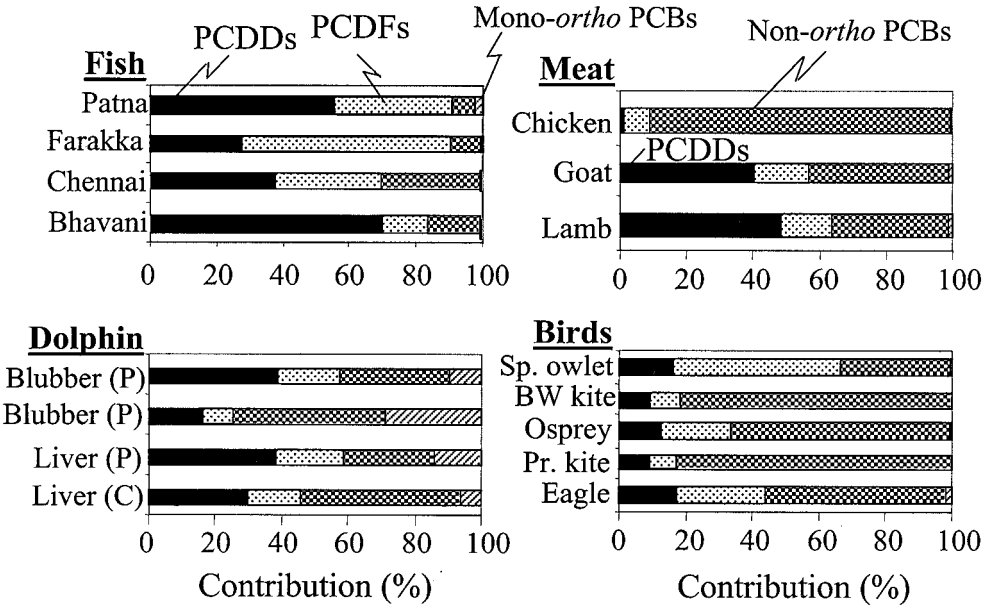

FIGURE 4. Relative contribution (%) of PCDDs, PCDFs, non-ortho- and mono-ortho-PCBs to TEQs in fish, meat, dolphin, and birds from India. P, Patna; C, Chappra.

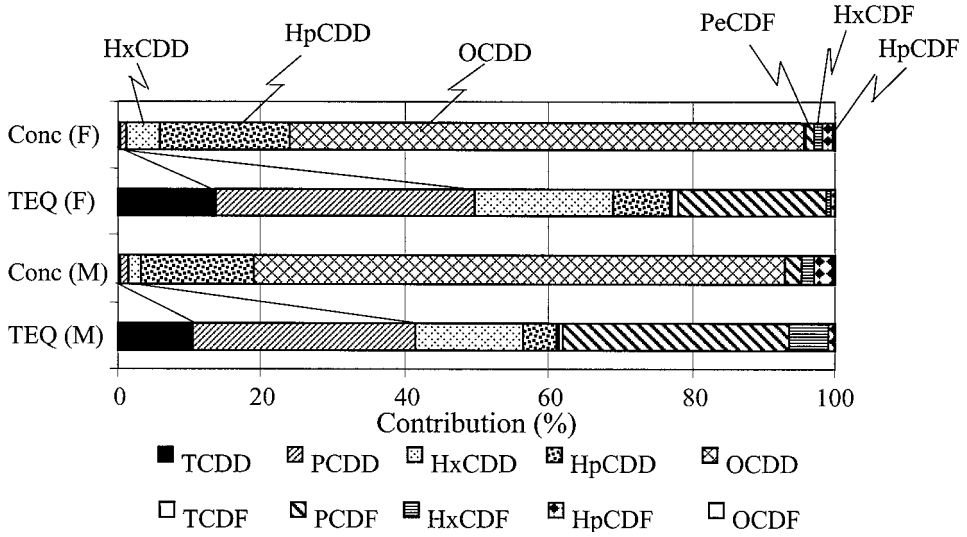

FIGURE 5. Relative concentrations (%) of PCDD/DF congeners to their total concentrations and their contribution (%) to TEQs in human adipose fat tissues from India.

including food habit. The major diet of Indians is of vegetable origin; therefore, the exposures to persistent pollutants such as PCDDs/DFs is expected to be minimal.

Toxic Equivalents. TEQs were estimated using WHO-TEFs (*18*). Concentrations of TEQs in fish and meat ranged from 1.9 to 18 and from 1.4 to 5.3 pg/g, fat wt, respectively (Figure 3). Concentrations of TEQs in Ganges River dolphin tissues ranged from 20 to 120 pg/g, fat wt. Birds showed elevated concentrations of TEQs ranging from 46 to 1100 pg/g, fat wt, in muscle and from 1000 to 1800 pg/g, fat wt, in liver (Figure 3). Concentrations of TEQs in humans were 14−46 pg/g, fat wt, in males and 16−56 pg/g, fat wt, in females (Figure 3).

The relative contribution of PCDDs, PCDFs, and PCBs to the concentrations of TEQs varied depending on the samples. PCDDs or PCDFs accounted for a major portion of TEQs in fishes from the Ganges River and Bhanavi Water Reservoir. However, non-ortho-PCBs contributed a significant portion of TEQs in fish from the Bay of Bengal (Figure 4). In goat and lamb meat, PCDDs and non-ortho-PCBs were the major contributors to TEQs (Figure 4). Similarly, in Ganges River dolphins, PCDDs/DFs and PCBs were the primary contributors to TEQ concentrations, followed by PCDFs and mono-ortho-PCBs. In birds, non-ortho-PCBs were the major contributors to TEQ concentrations followed by PCDFs > PCDDs > mono-ortho-PCBs. However, in the muscle of spotted owlet, TEQs were contributed in the following order: PCDF > non-ortho-PCBs > PCDD > mono-ortho-PCBs (Figure 4). In humans, PCDD/DFs were the major contributors to TEQs in most of the samples. In a few individuals, non-ortho-PCBs accounted for greater dioxin-like toxicity. The majority of TEQs in adipose tissues collected from Atlanta, GA, in 1986 were due to PCDDs (67%), whereas non-ortho-PCBs accounted for the second highest percentage (24%) (*40*). Congeners 12378-PCDD, 23478-PCDF, 2378-TCDD, and 123678-HxCDD contributed to the TEQs in humans (Figure 5).

International Comparison. Although it was expected that the concentrations of PCDDs/DFs in Indians would be minimal due to the predominance of a vegetarian diet, the concentrations in Indians were greater than those reported from China, Thailand, Cambodia, northern Vietnam, some

European countries, Korea, and Russia (Table 4 in Supporting Information). Furthermore, PCDD/DF concentrations in Indian adipose fat were comparable to or less than those reported during the 1980s in Canada, Finland, the United States, Germany, and Spain (*50*−*61*).

To our knowledge, this is the first report to document the extent of PCDD/DF contamination in humans and wildlife from India. The samples were collected randomly from a few sites; therefore, a systematic, nationwide monitoring is needed. This is highlighted by the presence of concentrations of PCDDs/DFs in Indian biota that are similar to or less than those reported for industrialized nations such as Japan and the United States but higher than those reported for several developing countries in Asia. TEQs contributed by PCDDs/DFs were greater than those of PCBs in several samples. In general, contamination by PCBs is relatively less in India. The profiles of PCDD/DF congeners in biological tissues including human fat tissues were similar to those found in PCP, although several additional sources such as chlorine bleaching of pulp, paper mill, and uncontrolled open burning of solid wastes have been identified as possible sources. The presence of several PCDD/DF congeners in humans and wildlife suggested the existence of multiple sources of PCDDs/DFs.

Acknowledgments

This study was supported by Japan Society for the Promotion of Science (JSPS) Fellowship awarded to K.S.K. (ID P00165).

Supporting Information Available

One table and three figures. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Baughman, R.; Meselson, M. *Environ. Health Perspect.* **1973**, *5*, 27−35.
(2) Zook, D. R.; Rappe, C. Environmental sources, distribution, and fate of polychlorinated dibenzodioxins, dibenzofurans, and related organochlorines. In *Dioxins and Health*; Schecter, A., Ed.; Plenum Press: New York, 1994; pp 79−113.
(3) Giesy, J. P.; Ludwig, J. P.; Tillitt, D. E. Dioxins, dibenzofurans, PCBs and similar chlorinated diaromatic hydrocarbons in and their effects on birds. In *Dioxins and Health*; Schecter, A., Ed.; Plenum Press: New York, 1994; pp 312−375.
(4) Schecter, A. *Environ. Health Perspect.* **1998**, *106*, 737−742.
(5) Liem, A. K. D.; Furst, P.; Rappe, C. *Food Addit. Contam.* **2000**, *17*, 241−259.
(6) Kannan, K.; Watanabe, I.; Giesy, J. P. *Toxicol. Environ. Chem.* **1998**, *67*, 135−146.
(7) Wittsiepe, J.; Schrey, P.; Ewers, U.; Selenka, F.; Wilhelm, M. *Chemosphere* **2000**, *40*, 1103−1109.
(8) Noren, K.; Meironyte, D. *Chemosphere* **2000**, *40*, 1111−1123.
(9) Dyke, P. H.; Foan, C.; Wenborn, M.; Coleman, P. J. *Sci. Total Environ.* **1997**, *207*, 119−131.
(10) Kannan, K.; Yamashita, N.; Imagawa, T.; Villeneuve, D. L.; Hashimoto, S.; Miyazaki, A.; Giesy, J. P. *Environ. Sci. Technol.* **2000**, *34*, 3560−3567.
(11) Gangal, N. D.; Bondre, S. S.; Ramanathan, P. S. *J. Chromatogr.* **2000**, *884*, 243−249.
(12) Nomani, A. A.; Ajmal, M. Ahmad, S. *Environ. Monit. Assess.* **1996**, *40*, 1−9.
(13) Kannan, K.; Oblisami, G. *Biol. Fertil. Soils* **1990**, *10*, 197−201.
(14) Anonymous. *Survey of Indian Industry*; The Hindu: 1995; p 448.
(15) Ahlborg, U. G.; et al. *Crit. Rev. Toxicol.* **1995**, *25*, 463−531.
(16) Safe, S. *Crit. Rev. Toxicol.* **1990**, *21*, 51−88.
(17) Safe, S. H. *Pharmacol. Ther.* **1995**, *67*, 247−281.
(18) Van den Berg, M.; Birnbaum, L.; Bosveld, A. T. C.; Brunstrom, B.; Cook, P.; Feeley, M.; Giesy, J. P.; Hanberg, A.; Hasegawa, R.; Kennedy, S. W.; Kubiak, T. J.; Larsen, J. C.; Rolaf van Leeuwen, F. X.; Liem, A. K. D.; Nolt, C.; Peterson, R. E.; Poellinger, L.; Safe, S.; Schrenk, D.; Tillitt, D.; Tysklind, M.; Younes, M.; Waern, F.; Zacharewski, T. *Environ. Health Perspect.* **1998**, *106*, 775−792.
(19) Kang, S.-Y.; Matsuda, M.; Kawano, M.; Wakimoto, T.; Min, B.-Y. *Chemosphere* **1997**, *35*, 2107−2117.
(20) Iseki, N.; Hayama, S.; Masunaga, S.; Nakanishi, J. *J. Environ. Chem.* **2000**, *10*, 817−831.
(21) Sakurai, T.; Kim, J. G.; Suzuki, N.; Masuo, T.; Li, D. Q.; Yao, Y.; Masunaga, S.; Nakanishi, J. *Chemosphere* **2000**, *40*, 627−640.
(22) Senthilkumar, K.; Iseki, N.; Masunaga, S.; Hayama, S.; Nakanishi, J. *Arch. Environ. Contam. Toxicol.* (in press).
(23) Feil, V. J.; Tiernan, T. *Organohalogen Compd.* **1997**, *33*, 353−354.
(24) Kannan, K.; Tanabe, S.; Tatsukawa, R.; Sinha, R. K. *Toxicol. Environ. Chem.* **1994**, *42*, 249−261.
(25) Senthilkumar, K.; Kannan, K.; Sinha, R. K.; Tanabe, S.; Giesy, J. P. *Environ. Toxicol. Chem.* **1999**, *18*, 1511−1520.
(26) Kannan, K.; Tanabe, S.; Tatsukawa, R. *Environ. Sci. Technol.* **1995**, *29*, 2673−2683.
(27) Toyoda, M.; Uchibe, H.; Yanagi, T.; Kono, Y.; Hori, T.; Iida, T. *J. Food Hyg. Soc. Jpn.* **1999**, *40*, 494−499.
(28) Harnly, M. E.; Petreas, M. X.; Flattery, J.; Goldman, L. R. *Environ. Sci. Technol.* **2000**, *34*, 1143−1149.
(29) Kannan, K.; Tanabe, S.; Ramesh, A.; Subramanian, A. N.; Tatsukawa, R. *J. Agric. Food Chem.* **1992**, *40*, 518−524.
(30) Loganathan, B. G.; Kannan, K.; Watanabe, I.; Kawano, M.; Irvine, K.; Kumar, S.; Sikka, H. C. *Environ. Sci. Technol.* **1995**, *29*, 1832−1838.
(31) Choi, J. W.; Matsuda, M.; Kawano, M.; Wakimoto, T.; Iseki, N.; Masunaga, S.; Hayama S.-I.; Watanuki, Y. *Organohalogen Compd.* **2000**, *46*, 507−509.
(32) Falandysz, J.; Yamashita, N.; Tanabe, S.; Tatsukawa, R.; Rucinska, L.; Mizera, T. Jakuczun, B. *Arch. Environ. Contam. Toxicol.* **1994**, *26*, 13−22.
(33) Guruge, K. S.; Tanabe, S.; Fukuda, M. *Arch. Environ. Contam. Toxicol.* **2000**, *38*, 509−521.
(34) Jones, P. D.; Hannah, D. J.; Buckland, S. J.; Day, P. J.; Leathem, S. V.; Porter, L. J.; Auman, H. J.; Sanderson, J. T.; Summer, C.; Ludwig, J. P.; Colborn, T. L.; Giesy, J. P. *Environ. Toxicol. Chem.* **1996**, *15*, 1793−1800.
(35) Koistinen, J.; Koivusaari, J.; Nuuja, I.; Vuorinen, P. J.; Paasivirta, J.; Giesy, J. P. *Environ. Toxicol. Chem.* **1996**, *16*, 1533−1544.
(36) Wu, W. Z.; Zhang, Q. H.; Schramm, K. W.; Xu, Y.; Kettrup, A. *Ecotoxicol. Environ. Saf.* **2000**, *46*, 252−257.
(37) Zimmermann, G.; Dietrich, D. R.; Schmid, P.; Schlatter, C. *Chemosphere* **1997**, *34*, 1379−1388.
(38) Senthilkumar, K.; Watanabe, M.; Kannan, K.; Subramanian, A. N.; Tanabe, S. *Toxicol. Environ. Chem.* **1999**, *71*, 221−239.
(39) Senthilkumar, K.; Kannan, K.; Subramanian, A. N.; Tanabe, S. *Environ Sci. Pollut. Res.* **2001**, *8*, 35−48.
(40) Patterson, D. G.; Todd, G. D.; Turner, W. E.; Maggio, V.; Alexander, L. R.; Needham, L. L. *Environ. Health Perspect.* **1994**, *102*, 195−204.
(41) LeBel, G. L.; Williams, D. T.; Benoit, F. M.; Goddard, M. *Chemosphere* **1990**, *21*, 1465−1475.
(42) Koistinen, J.; Koivusaari, J.; Nuuja, I.; Paasivirta, J. *Chemosphere* **1995**, *30*, 1671−1684.
(43) Iida, T.; Hirakawa, H.; Matsueda, T.; Nagayama, J.; Nagata, T. *Chemosphere* **1999**, *38*, 2475−2487.
(44) Duarte-Davidson, R; Harrad, S. J.; Allen, S.; Sewart, S.; Jones, K. C. *Arch. Environ. Contam. Toxicol.* **1993**, *24*, 100−107.
(45) Phillips, L. J.; Birchard, G. F. *Arch. Environ. Contam. Toxicol.* **1991**, *21*, 159−168.
(46) Ryan, J. J.; Masuda, Y.; Kostyniak, P. J. *Chemosphere* **1990**, *20*, 911−917.
(47) Ryan, J. J. *Chemosphere* **1986**, *15*, 1585−1593.
(48) Mes, J.; Davies, D. J.; Turton, D. *Bull. Environ. Contam. Toxicol.* **1982**, *28*, 97−104.
(49) Robinson, P. E.; Mack, G. A.; Remmers, J.; Levy, R.; Mohadjer, L. *Environ. Res.* **1990**, *53*, 175−192.
(50) Ryan, J. J.; Lizotte, R.; Lewis, D. *Chemosphere* **1987**, *16*, 1989−1996.
(51) Vartiainen, T.; Lampi, P.; Tuomisto, J. T.; Tuomisto, J. *Chemosphere* **1995**, *30*, 1429−1438.
(52) Thoma, H.; Mucke, W.; Kauert, G. *Chemosphere* **1990**, *21*, 433−442.
(53) Beck, H.; Eckart, K.; Mathar, W.; Wittkowski, R. *Chemosphere* **1989**, *18*, 507−516.
(54) Ryan, J.; Dewailly, E.; Ayotte, P.; Pedersen, H.; Mulvad, G. Hansen, J. *Organohalogen Compd.* **1996**, *30*, 247−250.
(55) Kim, Y.; Lee, S. Y.; Kim, M. *Organohalogen Compd.* **2000**, *48*, 34−36.
(56) Mamontova, E. A.; Mamontova, A. A.; Tarasova, E. N.; McLachlan, M. S. *Organohalogen Compd.* **1998**, *38*, 131−134.

(57) Gonzalez, M. J.; Jimenez, B.; Hernandez, L. M.; Caixach, J.; Rivera, J. *Chemosphere* **1993**, *27*, 97−104.
(58) Schuhmacher, M.; Domingo, J. L.; Llobet, J. M.; Lindstrom, G.; Wingfors, H. *Chemosphere* **1999**, *38*, 995−1004.
(59) Rappe, C.; Nygren, M.; Lindstrom, G.; Hansson, M. *Chemosphere* **1986**, *15*, 1635−1639.
(60) Stanley, J.; Kathy, E. B.; Onstot, J.; Sack, T. M. *Chemosphere* **1986**, *15*, 1605−1612.
(61) Phuong, N. T. N.; Hung, B. S.; Vu, D. Q.; Schecter, A. *Chemosphere* **1989**, *19*, 933−936.

Received for review January 19, 2001. Revised manuscript received May 8, 2001. Accepted June 5, 2001.

ES010555+