

Vertical Profile of Polychlorinated Dibenzo-*p*-dioxins, Dibenzofurans, Naphthalenes, Biphenyls, Polycyclic Aromatic Hydrocarbons, and Alkylphenols in a Sediment Core from Tokyo Bay, Japan

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Concentrations of polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), naphthalenes (PCNs), biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and nonylphenol (NP) were measured in a dated sediment core collected from Tokyo Bay, Japan, in order to study the history of contaminant inputs and fluxes. Concentrations of organochlorine compounds measured in this study increased gradually from the beginning of the early 1900s, reached a maximum in the early 1980s, and decreased steadily until the 1990s. The profile of isomer/congener compositions of PCDDs/DFs and PCNs varied with depth, which suggested that the sources of input of these compounds varied at different periods. The possible changing sources of PCDDs/DFs and PCNs to the environment are discussed in the context of the concentration trends and congener-specific data. The composition of PCB congeners was uniform at the top 40 cm, which corresponded to the period of usage of technical PCB mixtures, suggesting that the major single source of PCBs in sediments was technical preparations. All of the above organochlorines were detected in sediment sections collected at 90 cm depth, which corresponded to the early 1900s, suggesting the occurrence of these compounds in pre-industrial sediments. The vertical profile of PAHs was similar to that found for organochlorines with the highest concentrations occurring in the early 1980s. The vertical profile of NP concentrations was different from those observed for restricted compounds such as PCBs and PAHs. NP concentrations were greater in surface sediments (0–12 cm) than those in subsurface sediments (12–30 cm). In general, the profile of residues of organic compounds reflected production and usage trends of the respective compounds, although there was a time lag of a few years between peak periods of usage and deposition in coastal sediments. Improvements in emission controls in the late 1980s and the early 1990s appear to have been effective in reducing

the inputs of organic residues to the environment; however, the concentrations of several organochlorines in surface sediments are still greater than those found in sediments from the 1970s.

Introduction

Vertical profiles of residues in dated sediment cores have been used as historical records of pollution (1–3). Several studies have examined vertical profiles of persistent organic contaminants such as polychlorinated biphenyls (PCBs), dibenzo-*p*-dioxins (PCDDs), and dibenzofurans (PCDFs) and polycyclic aromatic hydrocarbons (PAHs) in sediment cores and found that the depositional histories of these compounds are often preserved in the sediment bed (1–5). For many restricted compounds such as PCBs, there is a subsurface peak in the sediment profile corresponding to the period of peak production and/or usage, followed by a slow decline to the sediment–water interface. Thus, these studies were useful to evaluate the effectiveness of legislative actions on the inputs of contaminants.

While studies have reported historical profiles of PCBs and PAHs, historical trends of polychlorinated naphthalenes (PCNs) and alkylphenols (APs), which are contaminants of emerging concern, are meager. A recent study reported concentrations of PCNs in a lacustrine sediment core in the U.K. (6). PCNs are a class of bioaccumulative chlorinated hydrocarbons that elicit toxic responses similar to PCDDs (7, 8). There is a growing body of evidence which suggests that PCN residues are fairly widespread in the environment (9, 10). APs such as nonylphenol (NP) and octylphenol (OP) are degradation products of alkylphenol ethoxylates (APEs). APEs are widely used as surfactants in detergents, paints, and emulsifying agents for industrial and agricultural applications (11). While several studies have reported their occurrence in aquatic environment (11), little is known about historical profiles of APs. Furthermore, few studies have reported historical profiles of contamination in sediment cores in Asian countries. In this study, we report vertical concentration profiles and fluxes of a wide variety of compounds such as PCDDs, PCDFs, PCNs, PCBs, PAHs, and APs in a sediment core collected from Tokyo Bay, Japan.

Materials and Methods

Sampling Location. Tokyo Bay, Japan, is surrounded by major cities such as Tokyo and Yokohama and is heavily contaminated by industrial and urban wastes. A sediment core was collected from Tokyo Bay (35°35' N and 139°55' E) using an acrylic tube (120 cm long and 11 cm i.d.) in May 1995. The depth of water column at this site was 14 m. Care was taken not to disturb the sediment surface by maintaining approximately 10–20 cm of clear bottom water above the core. The core was sectioned aboard ship immediately after collection using a stainless steel slicer. Sections were 2 cm for the initial 20 cm and 5 cm thereafter to a maximum depth of 93 cm. Each section was freeze-dried and stored at –20 °C until analysis.

Sedimentation. The estimated sedimentation rate using ²¹⁰Pb profiles (12) was based on the analysis of 80 sediment samples collected from Tokyo Bay and provided a reasonable

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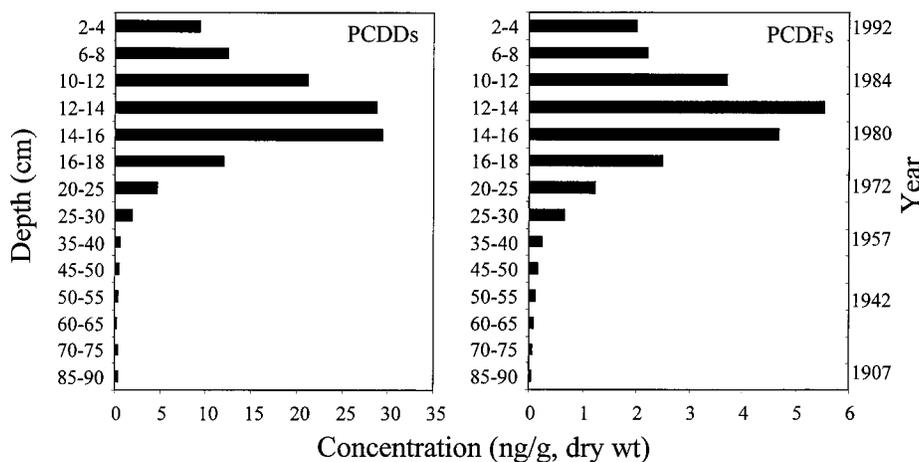


FIGURE 1. Vertical profile of PCDD and PCDF concentrations in a sediment core from Tokyo Bay.

estimation of the age of core sections. The sedimentation rate was determined to be $0.5 \text{ g cm}^{-2} \text{ yr}^{-1}$, which is approximately 1 cm/yr for the core sections. On the basis of this estimate, sediment core sections at depths of 0, 10, 20, 30, 40, and 50 cm correspond to approximately 1995, 1985, 1975, 1965, 1955, and 1945, respectively. The error associated with the dating could be as great as $\pm 5 \text{ yr}$, and adequate precautions have been exercised in our interpretations. Radioisotopes were not measured in the sediment core collected in this study.

Chemical Analysis

PCBs, PAHs, and APs. Sediments were Soxhlet extracted using dichloromethane (DCM) and hexane (3:1 v/v). Extracts were treated with acid-activated copper granules to remove sulfur. Concentrated extracts were fractionated using 10 g of activated Florisil packed in a glass column (10 mm i.d.). The first fraction (F1), eluted with 100 mL of hexane, contained PCBs. PAHs were eluted in the second fraction (F2) using 100 mL of 20% DCM in hexane. NP and OP were eluted in the third fraction (F3) with 100 mL of 50% DCM in methanol. PCBs and PAHs were quantified using a gas chromatograph interfaced with a high-resolution mass spectrometer (HRGC-HRMS). APs were quantified using a high-pressure liquid chromatograph (HPLC). Further details of the fractionation procedure and instrumental analyses have been described elsewhere (13). Using this method, PCNs were eluted in F1 and F2. PCDDs and PCDFs eluted in all three fractions. Therefore, PCNs, PCDDs, and PCDFs were extracted and determined by a separate analysis described below. In addition to instrumental analyses, these three florisil fractions were analyzed using *in vitro* bioassays. *In vitro* bioassay results are discussed elsewhere (14).

PCNs and PCDDs/DFs. A portion of freeze-dried sediments was Soxhlet extracted using toluene. The extract was concentrated and cleaned on a acidic silica/silica gel column by eluting with hexane. The hexane extract was concentrated to 1 mL and transferred to a carbon column packed with 1 g of activated carbon-impregnated silica gel. PCNs, PCDDs, and PCDFs were eluted with 200 mL of toluene and analyzed by a HRGC-HRMS. A Hewlett-Packard 6890 GC interfaced with a JEOL JMS-700 HRMS was used. Details of the instrumental conditions for PCN analysis have been described elsewhere (10). Separation of tetra- through hexachloro-DDs and -DFs was achieved by a fused silica capillary column SP-2331 (60 m \times 0.25 mm i.d.; Supelco, Bellefonte, PA) coated at $0.20 \mu\text{m}$ thickness. The column head pressure was kept at 200 kPa. Oven temperature was programmed from $80 \text{ }^\circ\text{C}$ (1 min) to $200 \text{ }^\circ\text{C}$ at $40 \text{ }^\circ\text{C/min}$, then to $260 \text{ }^\circ\text{C}$ at $1.5 \text{ }^\circ\text{C/min}$, and then to $270 \text{ }^\circ\text{C}$ at $0.5 \text{ }^\circ\text{C/min}$, which was held for 10 min.

Hepta- and octachloro-DDs and -DFs were separated on a DB-17 capillary column coated at $0.25 \mu\text{m}$ (30 m \times 0.25 mm i.d.). The column head pressure was kept at 120 kPa. The column oven temperature was programmed from $80 \text{ }^\circ\text{C}$ (1 min) to $160 \text{ }^\circ\text{C}$ at a rate of $40 \text{ }^\circ\text{C/min}$, and to $170 \text{ }^\circ\text{C}$ at $10 \text{ }^\circ\text{C/min}$, then to $250 \text{ }^\circ\text{C}$ at $4 \text{ }^\circ\text{C/min}$, to $280 \text{ }^\circ\text{C}$ at $6 \text{ }^\circ\text{C/min}$, and then to $296 \text{ }^\circ\text{C}$ at $4 \text{ }^\circ\text{C/min}$, which was held for 10 min. Injector and transfer line/ion source temperatures were held at 260 and $250 \text{ }^\circ\text{C}$, respectively. The mass spectrometer was operated at an EI energy of 70 eV, and the ion current was at $600 \mu\text{A}$. PCDD/DF congeners were monitored by selective ion monitoring (SIM) at the two most intensive ions at the molecular ion cluster. Calculated concentrations were reported as below the limit of detection if either the observed isotope ratio was not within $\pm 20\%$ of the theoretical ratio or peak area was not above the threshold amount (3 times the noise). The detection limits of individual PCDD, PCDF, or PCN congeners varied from 0.1 to 1 pg/g, depending on the sample size and relative responses. ^{13}C -Labeled tetra- through octachlorodibenzo-*p*-dioxins (ED-998, Cambridge Isotope Laboratories) were spiked as internal standards prior to Soxhlet extraction to estimate recoveries. Recoveries of T4CDD, P5CDD, H6CDD, H7CDD, and OCDD congeners through the analytical procedures were $110 \pm 20\%$, $102 \pm 16\%$, $87 \pm 12\%$, $90 \pm 22\%$, and $77 \pm 19\%$, respectively. Recoveries of tri-, tetra-, penta-, hexa-, hepta-, and octa-CN congeners were 70, 80, 90, 92, 94, and 82%, respectively. Non-*ortho*-coplanar PCBs were also measured using the analytical procedure described for PCNs (0.05–1 pg/g, dry wt) (10). PCN congener 1,2,3,4-T4CN was present in blank at trace amounts and, therefore, was not quantified.

Results and Discussion

PCDDs and PCDFs. Maximum concentrations of total PCDDs and PCDFs were detected at depths of 14–16 and 12–14 cm, respectively. These sections of the core approximately corresponded to the early 1980s (Figure 1; Table 1). The greatest concentrations of PCDDs and PCDFs in sediments were 29.4 and 5.5 ng/g, dry wt, respectively. The vertical profile of PCDDs/DFs was characterized by fairly uniform concentrations from the depth of 50 cm (\approx year 1945) to 90 cm (\approx year 1905). PCDD/DF concentrations increased dramatically from the 1950s to the early 1980s and then decreased slightly from the late 1980s to the early 1990s. This profile is similar to those reported for a sediment core from the Baltic Sea (15) and the Great Lakes (16). This profile corresponds with an increase in industrial activities until the 1980s followed by stringent regulations on industrial emissions of PCDDs/DFs. Low concentrations of PCDDs/DFs were detected at depths of 85–90 cm, which corresponded to the

TABLE 1. Estimated Fluxes ($\text{ng cm}^{-2} \text{ yr}^{-1}$) and Concentrations (ng g^{-1} , dry wt) of Organochlorines, PAHs, and Nonylphenol in Sediments of Tokyo Bay, Japan^a

depth (cm)	time interval represented	PCDDs		PCDFs		PCNs		PCBs		PAHs		NP	
		concn	flux	concn	flux	concn	flux	concn	flux	concn	flux	concn	flux
0–2	1993–1995	na ^b	na	na	na	na	na	43.8	21.9	360	180	4810	2405
2–4	1991–1993	9.31	4.66	2.02	1.01	1.81	0.91	29.1	14.6	581	291	5540	2770
10–12	1983–1985	21.2	10.6	3.71	1.86	3.25	1.63	77.1	38.6	1350	675	3430	1715
12–14	1981–1983	28.8	14.4	5.53	2.77	4.11	2.06	151	75.5	2010	1005	3230	1615
14–16	1981–1979	29.4	14.7	4.67	2.34	4.43	2.22	137	68.5	1610	805	1960	980
20–25	1970–1975	4.63	2.32	1.22	0.61	4.07	2.04	17.3	8.65	1340	670	340	170
45–50	1945–1950	0.42	0.21	0.17	0.09	0.49	0.25	6.2	3.1	665	333	<10	<5
85–90	1905–1910	0.39	0.2	0.034	0.017	0.2	0.1	3.39	1.7	65	32.5	<10	<5

^a Flux estimates and concentrations are presented for only selected depth layers. Flux estimates are based on the sedimentation rate of $0.5 \text{ ng cm}^{-2} \text{ yr}^{-1}$ (12). ^b na, not available.

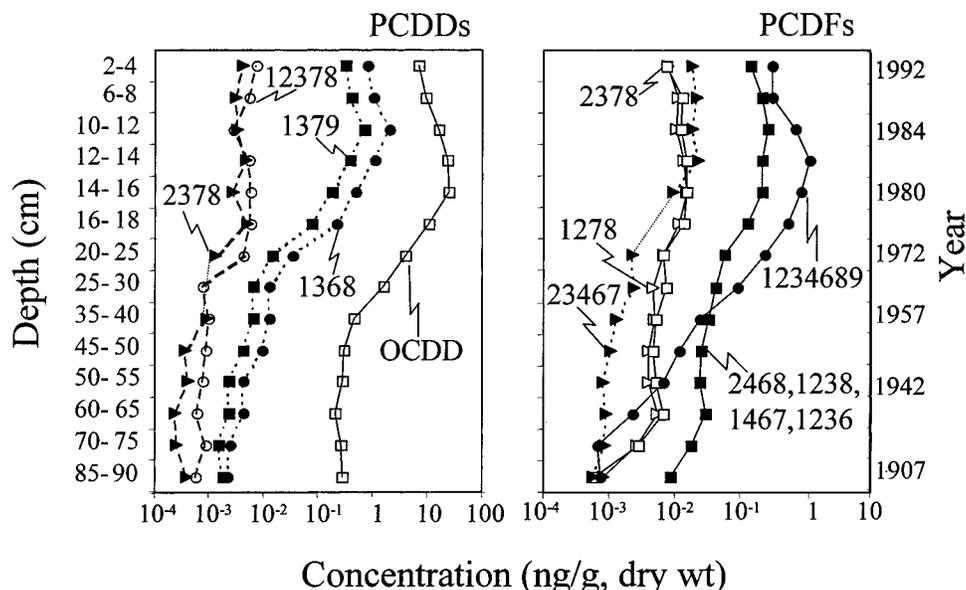


FIGURE 2. Vertical profile of selected PCDD and PCDF congeners in a sediment core from Tokyo Bay.

early 1900s. The concentrations of PCDDs/DFs detected at these depths were 100–150 times less than the greatest concentrations measured. The presence of PCDDs/DFs in sediments that predate the 1900s has been reported earlier (15, 17). The presence of PCDDs/DFs in deep sediment cores from the early 1900s support the evidence for the existence of PCDDs/DFs in the pre-industrial period (18).

In general, PCDD concentrations were 5-fold (range: 2.5–11) greater than those of PCDFs throughout the core. The vertical profile of PCDD/DFs suggests different depositional histories for the various congeners (Figure 2). Although differences in the physicochemical (mobility, solubility, etc.) and biological (degradation, etc.) properties may alter their congener profile, these processes play a minor role under anoxic conditions in sediments. Analysis of water from Tokyo Bay revealed the presence of greater concentrations of PCDDs than of PCDFs (19). Earlier studies have reported the preservation of congener profiles of various organochlorine compounds in sediment cores (1–3). Differences in congener profiles at various depths may imply the presence of several sources. Among PCDD homologues, OCDD accounted for 70–85% of the total concentrations. The proportion of OCDD in total PCDD concentrations remained relatively uniform as compared to that of hexachlorodibenzo-*p*-dioxins (H6CDD), which were higher in deeper layers. A high percentage of OCDD and H7CDD in total PCDD/DF concentrations suggested pentachlorophenol (PCP) (20) as a major source of PCDDs/DFs found in the sediment. This is likely due to the fact that the PCP was used as an herbicide

in rice cultivation and in other applications such as lumber treatment. For agricultural purposes alone, 170 000 ton of PCP active ingredient were used in Japan during the 1960s and the early 1970s. A similar profile of PCDD/DF composition was found in a sediment core from Lake Shinji in Japan (21). The composition of tetrachlorodibenzo-*p*-dioxins (T4CDD) was greater in surface layers than in deeper layers. The greater proportion of T4CDD in surface layers has been attributed to the use of chloronitrofen (CNP). CNP has been used in Japanese agriculture since the 1970s as a replacement for PCP (22). T4CDD and P5CDD are relatively abundant in CNP as compared to those in PCP. Relatively higher proportions of T4CDD and P5CDD in surface layers of sediments suggested that the source of PCDDs/DFs was CNP. Among PCDFs, OCDF accounted for 30–52% of total PCDF concentrations from surface layer for up to 55 cm, while tetrachlorodibenzofuran (T4CDF) accounted for a major proportion (25–32%) at 60–90 cm depth. The percentage of H7CDF in total PCDF concentrations decreased with increasing depth, while P5CDF and T4CDF increased in surface layers (Figure 2).

Both 2,3,7,8-substituted and non-2,3,7,8-substituted congeners of PCDDs/DFs were measured in sediment cores. 2,3,7,8-Substituted PCDD congeners accounted for 74–91% of the total PCDD concentrations in core sections while 2,3,7,8-substituted PCDFs accounted for 42–68% of the total PCDF concentrations. Congener-specific data for PCDDs/DFs in sediment cores provided some information about the sources. Congeners such as OCDD and 1,2,3,4,6,8,9-H7CDF

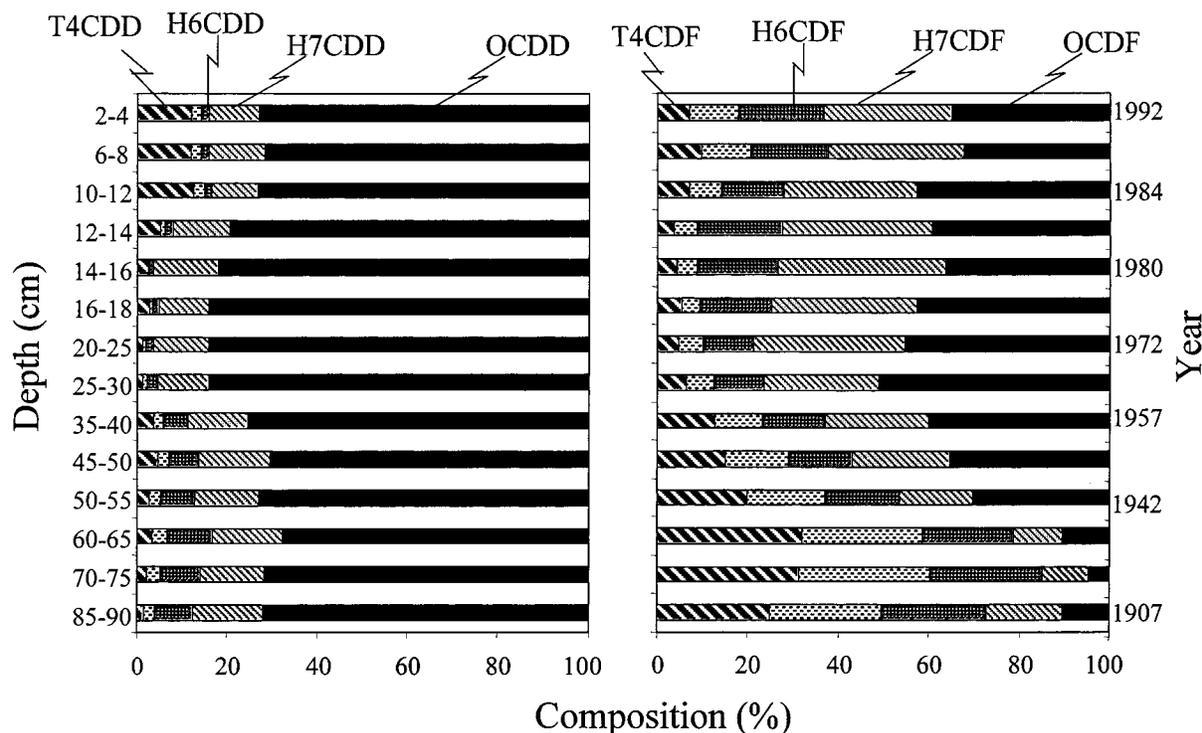


FIGURE 3. Composition of PCDD and PCDF homologues in a sediment core from Tokyo Bay.

are characteristic of PCP whereas those of 1,3,6,8- and 1,3,7,9-T4CDDs are indicative of sources originating from CNP and municipal solid waste incineration (MSWI) (22, 23). 1,3,6,8- and 1,3,7,9-T4CDDs accounted for >60% of the T4CDDs throughout the core and accounted for 96% of the T4CDDs at the 10–12 cm depth. 3,4,6,7-T4CDF and 2,3,4,6,7-P5CDF are marker congeners for MSWI-related sources (23). 2,3,7,8- and 1,2,7,8-T4CDFs, total T4CDF, and H6CDD are suggestive of emissions from chlorine bleaching of pulp (24). Subsurface maximum concentration for OCDD and 1,2,3,4,6,8,9-H7CDF predate the maximum loading of congeners originating from CNP (Figure 3). Variations among individual congener histories (Figure 3) suggest the presence of independent emission sources (PCP, CNP, MSWI, pulp mill, etc.) (25). PCDD/DF congeners that are indicative of MSWI- and pulp mill-related sources increased in slices at 40 cm depth, which corresponds to the 1950s, and leveled off at the surface layers. Although the source signature implies that PCP has been the major source of PCDDs/DFs found in Tokyo Bay, several other sources such as municipal sewage sludge and MSWI can produce OCDD as the primary constituent along with other more chlorinated dioxin congeners (26). The historical profile of individual PCDD/DF congeners suggest continuing input of these congeners from certain sources such as MSWI, and municipal sewage.

PCNs. The vertical profile of PCNs was similar to that found for PCDDs/DFs (Figure 4). The profile was characterized by lesser concentrations in deeper layers, followed by an exponential increase to a subsurface peak and a gradual decrease to the surface. The maximum PCN concentration of 4.4 ng/g, dry wt, was found in the 14–16-cm section, which corresponded to the year 1980. However, increases in concentrations of PCNs in sediments were observed as early as the 1960s (25–30 cm), which predates those for PCBs (Figure 12). Sediment core taken from a lake in the U.K. showed that the PCN maximum predated the PCB maximum by approximately 20 yr (6). Concentrations of PCNs in the deepest sections of sediment core were 25-fold less than the maximum concentrations observed. Occurrence of PCNs at 90 cm depth was similar to that reported for PCDDs/DFs

and suggests inputs in the pre-industrial period. Possible sources and reasons for the occurrence of PCDDs/PCDFs in sections of sediment cores that dated pre-1920s have been discussed earlier (3). A likely source of PCNs in sediments originating in the early 1900s is combustion of wood or coal, as has been suggested for PCDDs/DFs.

Tri- and tetra-CN congeners accounted for greater than 80% of the total PCN concentrations at depths below 50 cm and their composition increased gradually with depth. This profile is most similar to Halowaxes 1001 and 1099, which are technical preparations of PCNs containing predominant proportions of tri- and tetra-CN congeners. Major sources of PCNs in the environment were technical Halowax mixtures, MSWI, and technical PCB mixtures (27, 28). Information about the production of technical PCNs in Japan is not known. Penta-CN was the predominant congener in surface sediments, accounting for greater than 35% of the total PCN concentrations (Figure 4). Greater composition of P5CNs is suggestive of inputs from higher chlorinated PCN mixtures such as Halowaxes 1013 and 1014 (29). The increase in the composition of P5CN and H6CN in total PCN concentrations at surface layers may imply exposure to Halowax 1014. However, there were variations in the vertical profiles of individual PCN isomers (Figure 5), which suggest input of PCNs from several sources, as has been observed for PCDDs/DFs. H6CN congeners 1,2,4,5,6,8/1,2,4,5,7,8- are the predominant H6CN congeners in Halowax 1014, accounting for 42% of the total H6CN (28). Fly ash arising from municipal solid waste incinerators contain predominantly 1,2,3,4,6,7/1,2,3,5,6,7-H6CNs (13–74% of the total H6CN). Among P5CNs, 1,2,4,5,8 is the major congener present in Halowax 1014 (26% of the total P5CNs) while fly ash contains predominantly 1,2,3,5,7/1,2,4,6,7 (29% of the total P5CNs) (27). The vertical profile of these marker congeners suggested a greater contribution from MSWI (fly ash) in deeper layers. Degradation of PCN congeners substituted at 1, 4, 5, or 8 (peri-positions) may alter profiles of PCN homologue composition. Variations in the composition of these congeners in sediment core sections compared to those in source materials suggest exposure to several other sources of PCNs and possible weathering of congeners.

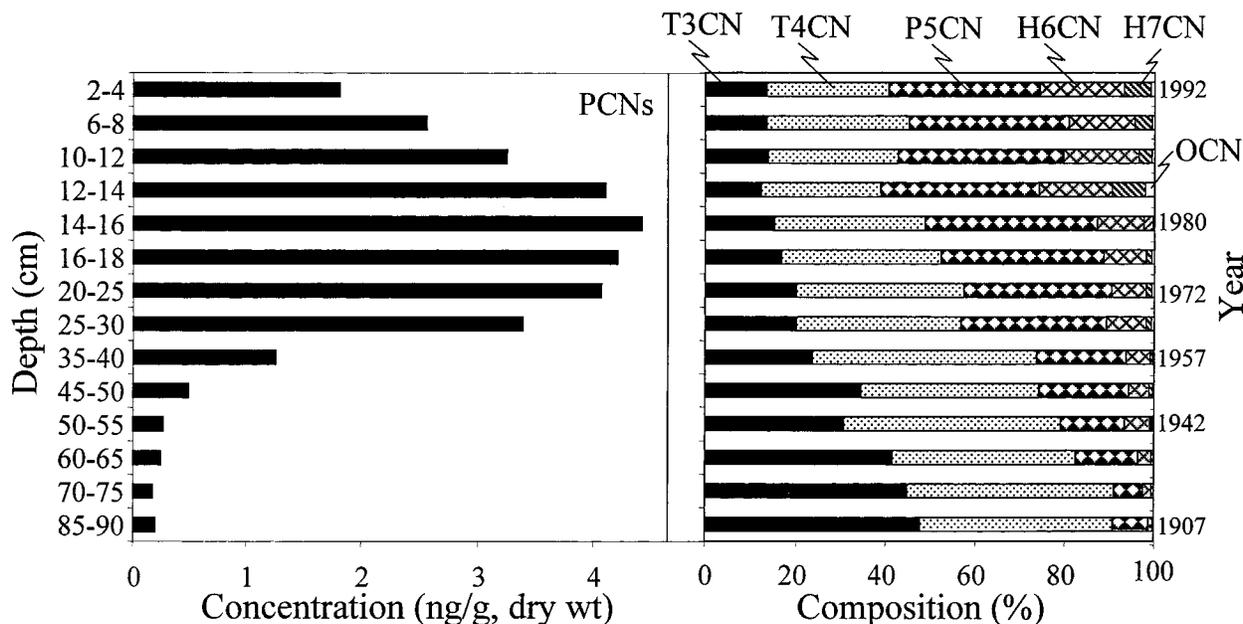


FIGURE 4. Vertical profile of PCN concentrations and homologue composition in a sediment core from Tokyo Bay.

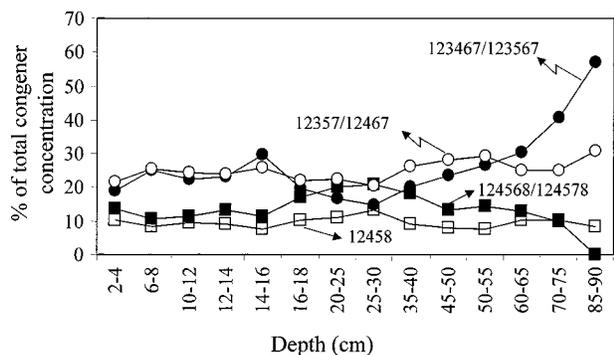


FIGURE 5. Vertical profile of selected PCN congeners in a sediment core from Tokyo Bay.

Concentrations of PCNs in surface sediments were approximately 5–7 times less than those of PCDDs but similar to those of PCDFs. In core sections below 25 cm, concentrations of PCNs and PCDDs/DFs varied within a factor of 2. Concentrations of total PCNs in sediments were less than those reported for riverine sites in Sweden and the Baltic Sea (30) and the Tsurumi River, Japan (27, 28), and the Detroit River, United States (Kannan, unpublished).

PCBs. Concentrations of PCBs increased from 2 to 6 ng/g, dry wt, from the late 1940s to the 1960s, increased dramatically from the late 1970s to the early 1980s, and then gradually declined (Figure 6). This trend is similar to that found in human adipose tissue from Japan, in which PCB residues appeared in human tissues as early as the 1940s, peaked in the early 1980s, and then slowly declined (31). PCBs were produced in Japan since the early 1950s, and the production increased until the early 1970s. Prior to the production in the 1950s, PCBs were imported into Japan. Despite a ban on the production of PCBs in Japan in 1972, the sediment core profile and trend studies using archived human tissues suggest the existence of peak concentrations in the early 1980s. This may suggest a time lag between peak periods of production and usage and the deposition to coastal marine environment by particulate transport and deposition, which are controlled by hydraulic residence times and particle settling velocities. The reduced concentrations observed in the surface sediments is largely the response to controls on

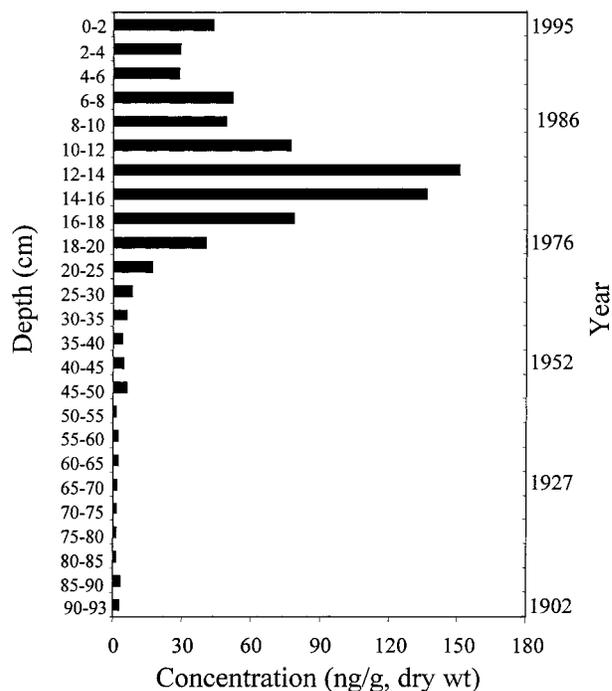


FIGURE 6. Vertical profile of PCB concentrations in a sediment core from Tokyo Bay.

the manufacture, use, and disposals of PCBs, which resulted in their decreased input to the bay.

The greatest PCB concentration (150 ng/g, dry wt), measured at a depth of 12–14 cm, was 3-fold greater than that found in the surface layer. The highest PCB concentration postdates those observed for PCNs and PCDDs, for which peak concentrations were found in the 14–16-cm section. Similar to PCNs and PCDDs/DFs, PCBs were found in sediment sections collected at 90 cm, which corresponded to the early 1900s. Interestingly, PCBs in the deepest sections were dominated by T3CB and T4CB (Figure 7). Lesser chlorinated congeners are more soluble and mobile and would diffuse from the subsurface peak. A similar observation of the presence of lesser chlorinated PCBs in sediments dated to have been deposited in the pre-1900s has been made in

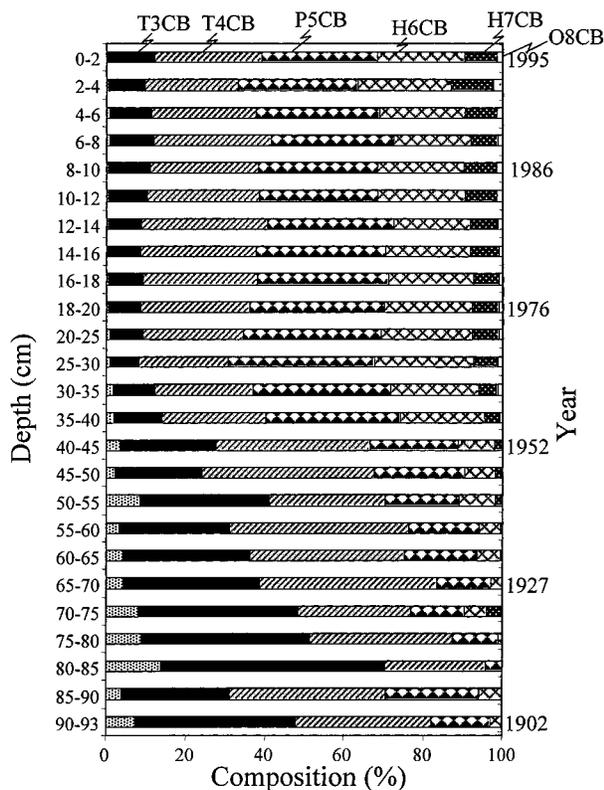


FIGURE 7. Composition of PCB congeners in a sediment core from Tokyo Bay.

a rural lake sediment core in the U.K. (6). Neither PCDDs/DFs nor PCBs were present in the solvent blanks. Although the possibility of smearing along the acrylic tube margins while sampling has to be considered, the mass of smearing sediment is probably not significant. The profile and pattern of PCB congeners was different at the bottom of the core. Contamination from smearing would not be expected to create pattern and profile changes. The presence of these compounds in sediments that predate the industrial period suggests selective movement/percolation of less chlorinated congeners and/or the existence of an unknown (possibly natural) source. Potential natural sources of PCBs have been discussed previously (6, 15). PCBs found deep in Tokyo Bay sediments validate earlier observations of the occurrence of PCBs in pre-1900 sediments.

The major source of PCBs in sediments is technical PCB preparations such as Kanechlors produced in Japan. The PCB congener pattern in the top 50 cm of sediment core was dominated by T4CB, P5CB, and H6CB, collectively accounting for 75–80% of the total PCBs (Figure 7). The uniformity in the pattern of PCB congeners in the top 50 cm suggests the existence of a single major source. It also suggests that mineralization processes are very slow and that the sediment redistribution of these compounds is of minor significance in sediments.

PAHs. Total concentrations of 16 priority PAHs varied from 38 to 2000 ng/g, dry wt. The highest concentration was observed at a depth of 12–14 cm, and the lowest was at a depth of 90–93 cm, the bottom-most section taken for this study. The PAH concentration increased exponentially from background concentrations to a subsurface maximum corresponding to the 1970s and early 1980s when fossil fuel consumption was increasing globally. PAH concentrations decreased thereafter to the sediment–water interface (Figure 8). This suggests that PAH inputs to Tokyo Bay have declined in recent years. In the past 10 yr, PAH inputs to Tokyo Bay have declined by more than 5-fold as compared to that in

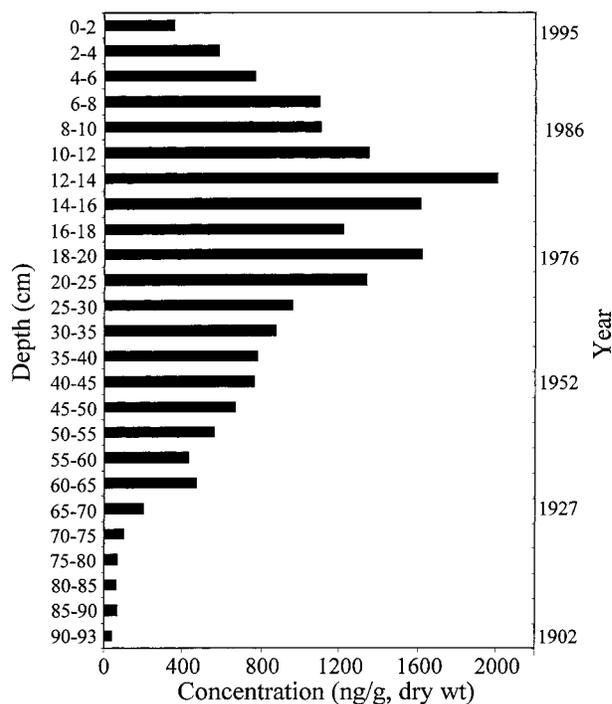


FIGURE 8. Vertical profile of PAH concentrations in a sediment core from Tokyo Bay.

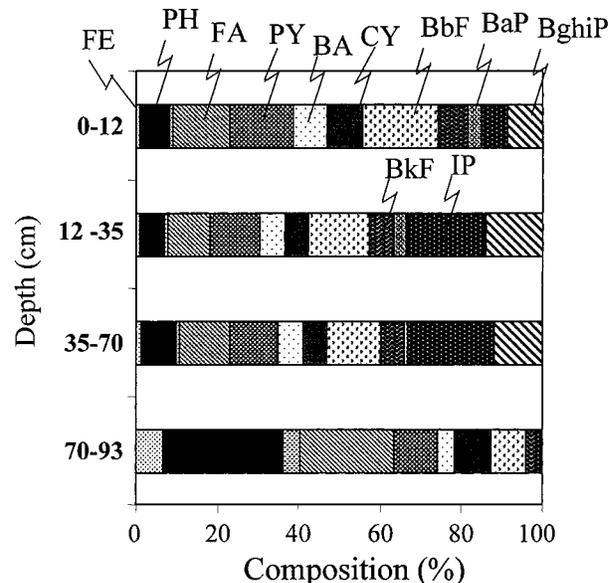


FIGURE 9. Composition of PAH compounds at selected depth intervals in sediment core from Tokyo Bay: FE, fluorene; PH, phenanthrene; FA, fluoranthene; PY, pyrene; BA, benz[a]anthracene; CY, chrysene; BbF, benzo[b]fluoranthene; BkF, benzo[k]fluoranthene; BaP, benzo[a]pyrene; IP, indeno[1,2,3-*cd*]pyrene; BghiP, benzo[ghi]perylene.

peak periods of input (early 1980s) but are still an order of magnitude above the pre-industrial concentrations. As with organochlorines, the reduction in PAH concentrations during the past decade has been due partly to improvements in emission controls.

The profile of individual PAH compounds varied with depth (Figure 9). The topmost (0–10 cm) and the deepest sections (70–93 cm) were dominated by 3- and 4-ring PAHs, whereas 5- and 6-ring PAHs contributed a major percentage to total PAHs in midsections (12–70 cm). In general, fluoranthene, pyrene, benzo[b]fluoranthene, and indeno-

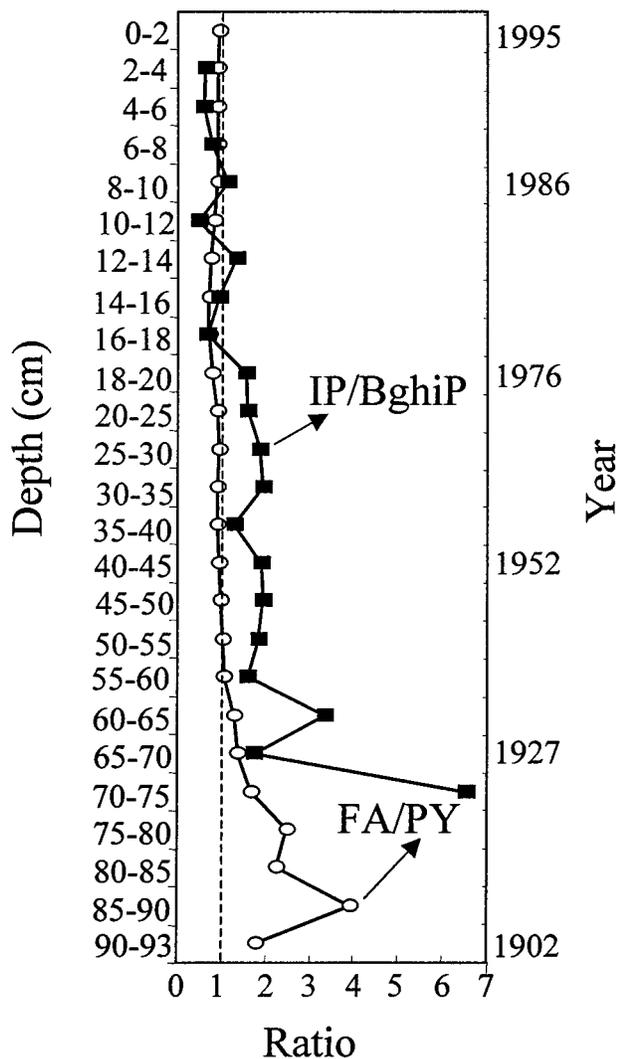


FIGURE 10. Ratios of fluoranthene to pyrene (FA/PY) and indeno[1,2,3-*cd*]pyrene to benzo[*ghi*]perylene (IP/BghiP) in a sediment core from Tokyo Bay.

[1,2,3-*cd*]pyrene were the important contributors to PAH burden in sediments. Benzo[*b*]fluoranthene was the most abundant (among 16 PAHs) in the top 12 cm. It accounted for 15–20% of the total PAH concentrations. In deeper layers (12–70 cm), indeno[1,2,3-*cd*]pyrene accounted for a major proportion of the total PAH concentrations. Phenanthrene and fluoranthene dominated at depths greater than 70 cm. Changes in the PAH pattern may reflect changes in the sources of PAHs such as coal, oil, gas, and petroleum combustion and the effect of combustion conditions. PAHs originate mainly from petrogenic and pyrolytic sources. The use of ratios of PAH components of the same molecular mass has been established as a method of inferring PAH sources and diagenesis of PAHs (32). For instance, a ratio of fluoranthene to pyrene concentrations (Fluo/Py) greater than 1.0 is characteristic of a pyrolytic origin whereas ratios less than 1.0 are characteristic of petroleum hydrocarbons. Similarly, a ratio of indeno[1,2,3-*cd*]pyrene to benzo[*ghi*]perylene (I123cdP/BghiP) greater than 1.0 suggests combustion sources, whereas I123cdP/BghiP ratios less than 1.0 imply petrogenic sources. Nevertheless, for both the ratios the limits between the two processes are not precise (32, 33). The Fluo/Py ratios for sediment core samples were less than 1 for depths up to 50 cm and then increased downward. Similarly, the ratios of I123cdP/BghiP increased gradually downward and were less than 1 for depths of 0–20 cm (Figure 10). A downcore

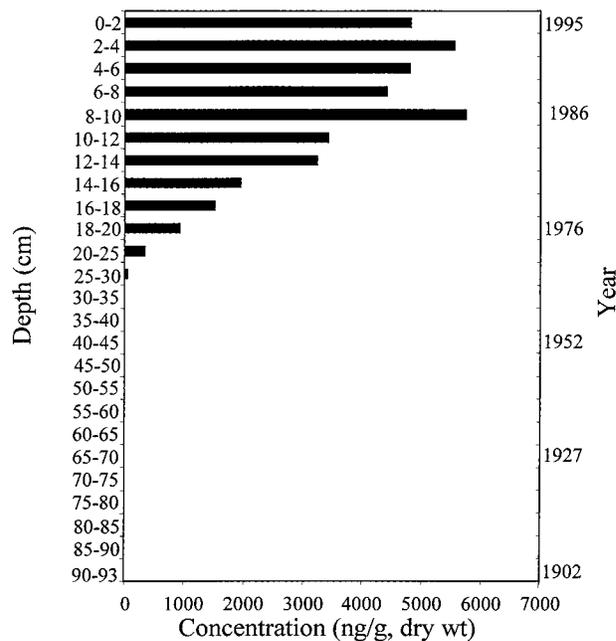


FIGURE 11. Vertical profile of nonylphenol concentrations in a sediment core from Tokyo Bay.

increase in the proportions of both indeno[1,2,3-*cd*]pyrene and fluoranthene, particularly at depths 60–93 cm, suggests that combustion related sources predominated until the 1930s, whereas both petrogenic and pyrolytic contributed to PAH sources after the 1930s. The existence of PAHs in sediments that date back to the early 1900s can be explained by inputs associated with fossil fuel consumption for over 100 yr in addition to possible natural formation.

Alkylphenols. The vertical distribution of NP concentrations in sediment was different from that of PAHs and organochlorine compounds analyzed in this study. Concentrations of NP in surface sediments were an order of magnitude greater than those of PAHs and PCBs. Concentrations of NP ranged from <10 to 5540 ng/g, dry wt. NP was detected only at depths above 30 cm, which corresponded to the mid-1960s (Figure 11). The vertical profile of NP increased gradually from the mid 1960s, peaked in the mid 1980s, and remained steady until the mid 1990s. Great NP concentrations in surface layers suggest recent inputs. APs have been used in cleaning products and industrial processing for 30–40 yr (34). Octylphenol (OP) concentrations in the sediment core ranged from <10 to 190 ng/g, dry wt. OP concentrations were 5–50-fold less than those of NP. NP and OP concentrations were significantly correlated ($p < 0.05$). The ratios of NP/OP showed a downward decrease with depth in sediment cores suggesting either greater persistence of NP or decreased inputs of OP over time.

Summary

Overall, the current concentrations of measured organochlorines and PAHs in surface sediments are approximately 3–5-fold less than the maximum concentrations found in the 1980s (Figure 12). NP concentrations appear to have reached a steady state. The current flux of NP (2405 ng cm⁻² yr⁻¹) in Tokyo Bay is approximately an order of magnitude higher than that of PAHs (180 ng cm⁻² yr⁻¹) and 2 orders of magnitude greater than that of PCBs (22 ng cm⁻² yr⁻¹) (Table 1). While NP concentrations and profile were correlated with those of OP, there was no correlation between NP and other contaminants examined (Table 2). PCDD concentrations and profiles were significantly correlated with those of PCDFs

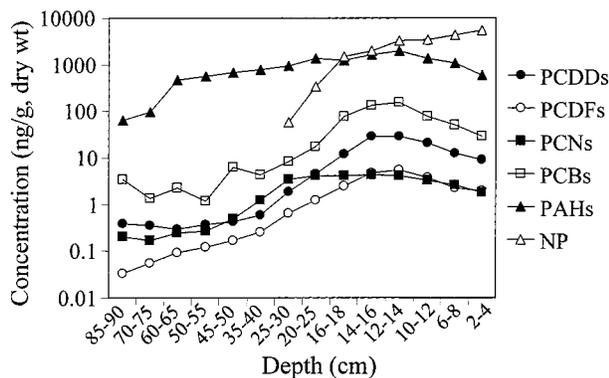


FIGURE 12. Trends in the concentrations of PCDDs, PCDFs, PCNs, PCBs, PAHs, and nonylphenol in a sediment core from Tokyo Bay. Concentrations in selected depths have been presented.

TABLE 2. Correlation Coefficients (r^2) for Concentrations and Profiles of PCDDs, PCDFs, PCNs, PCBs, PAHs, and NP in a Sediment Core from Tokyo Bay, Japan

	PCDDs	PCDFs	PCNs	PCBs	PAHs	NP
PCDDs	1	0.98	0.55	0.96	0.70	0.4
PCDFs		1	0.61	0.95	0.75	0.43
PCNs			1	0.56	0.8	0.17
PCBs				1	0.72	0.29
PAHs					1	0.18
NP						1

and PCBs. PCNs profiles and concentrations were significantly correlated with those of PAHs. This suggests a relationship between their sources. Formation of PCNs from PAHs in MSWI has been reported recently (35).

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Literature Cited

- Hites, R. A.; Laflamme, R. E. *Science* **1977**, *198*, 829–831.
- Eisenreich, S. J.; Capel, P. D.; Robbins, J. A.; Bourbonniere, R. *Environ. Sci. Technol.* **1989**, *23*, 1116–1126.
- Gevao, B.; Jones, K. C.; Hamilton-Taylor, J. *Sci. Total Environ.* **1998**, *215*, 231–242.
- Wong, C. S.; Sanders, G.; Engstrom, D. R.; Long, D. T.; Swackhamer, D. L.; Eisenreich, S. J. *Environ. Sci. Technol.* **1995**, *29*, 2661–2672.
- Muir, D. C. G.; Omelchenko, A.; Grift, N. P.; Savoie, D. A.; Lockhart, W. L.; Wilkinson, P.; Brunskill, G. J. *Environ. Sci. Technol.* **1996**, *30*, 3609–3617.
- Gevao, B.; Harner, T.; Jones, K. C. *Environ. Sci. Technol.* **2000**, *34*, 33–38.
- Blankenship, A.; Kannan, K.; Villalobos, S.; Villeneuve, D. L.; Falandysz, J.; Imagawa, T.; Jakobsson, E.; Giesy, J. P. *Environ. Sci. Technol.* **2000**, *34*, 3153–3158.

- Villeneuve, D. L.; Khim, J. S.; Kannan, K.; Falandysz, J.; Blankenship, A. L.; Giesy, J. P. *Arch. Environ. Contam. Toxicol.* In press.
- Harner, T.; Kylin, H.; Bidleman, T. F.; Halsall, C.; Strachan, W. M. J. *Environ. Sci. Technol.* **1998**, *32*, 3257–3265.
- Kannan, K.; Yamashita, N.; Imagawa, T.; Decoan, W.; Khim, J. S.; Day, R. M.; Summer, C. L.; Giesy, J. P. *Environ. Sci. Technol.* **2000**, *34*, 566–572.
- Maguire, R. J. *Water Qual. Res. J. Can.* **1999**, *34*, 37–78.
- Matsumoto, E. *Chikyu Kagaku* **1983**, *17*, 27–32 (in Japanese).
- Khim, J. S.; Kannan, K.; Villeneuve, D. L.; Koh, C. H.; Giesy, J. P. *Environ. Sci. Technol.* **1999**, *33*, 4199–4205.
- Kannan, K.; Villeneuve, D. L.; Yamashita, N.; Imagawa, T.; Hashimoto, S.; Miyazaki, A.; Giesy, J. P. *Environ. Sci. Technol.* **2000**, *34*, 3568–3573.
- Kjeller, L.-O.; Rappe, C. *Environ. Sci. Technol.* **1995**, *29*, 346–355.
- Pearson, R. F.; Swackhamer, D. L.; Eisenreich, S. J.; Long, D. T. *Environ. Sci. Technol.* **1997**, *31*, 2903–2909.
- Hashimoto, S.; Wakimoto, T.; Tatsukawa, R. *Chemosphere* **1990**, *21*, 825–835.
- Alcock, R. E.; McLachlan, M. S.; Johnston, A. E.; Jones, K. C. *Environ. Sci. Technol.* **1998**, *32*, 1580–1587.
- Yamashita, N.; Imagawa, T.; Miyazaki, A. *Organohalogen Compd.* **1997**, *32*, 204–209.
- Hagenmaier, H.; Brunner, H. *Chemosphere* **1987**, *16*, 1759–1764.
- Masunaga, S.; Yao, Y.; Ogura, I.; Nakai, S.; Kanai, Y.; Yamamuro, M.; Nakanishi, J. *Organohalogen Compd.* **1999**, *43*, 383–386.
- Masunaga, S.; Nakanishi, J. *Organohalogen Compd.* **1999**, *41*, 41–44.
- Yasuhara, A.; Ito, H.; Morita, M. *Environ. Sci. Technol.* **1987**, *21*, 971–979.
- Macdonald, R. W.; Ikonomou, M. G.; Paton, D. W. *Environ. Sci. Technol.* **1998**, *32*, 331–337.
- Bright, D. A.; Cretney, W. J.; Macdonald, R. W.; Ikonomou, M. G.; Grundy, S. L. *Environ. Toxicol. Chem.* **1999**, *18*, 1097–1108.
- Loganathan, B. G.; Kannan, K.; Watanabe, I.; Kawano, M.; Irvine, K.; Kumar, S.; Sikka, H. C. *Environ. Sci. Technol.* **1995**, *29*, 1832–1838.
- Imagawa, T.; Yamashita, N.; Miyazaki, A. *J. Environ. Chem.* **1993**, *3*, 221–230 (in Japanese).
- Imagawa, T. *J. Environ. Chem.* **1994**, *4*, 671–676 (in Japanese).
- Kannan, K.; Imagawa, T.; Blankenship, A.; Giesy, J. P. *Environ. Sci. Technol.* **1998**, *32*, 2507–2514.
- Järnberg, U.; Asplund, L.; de Wit, C.; Egeback, A. L.; Wideqvist, U.; Jakobsson, E. *Arch. Environ. Contam. Toxicol.* **1997**, *32*, 232–245.
- Loganathan, B. G.; Tanabe, S.; Hidaka, Y.; Kawano, M.; Hidaka, H.; Tatsukawa, R. *Environ. Pollut.* **1993**, *81*, 31–39.
- Yunker, M. B.; Snowdon, L. R.; Macdonald, R. W.; Smith, J. N.; Fowler, M. G.; Skibo, D. N.; McLaughlin, F. A.; Dantushevskaya, A. I.; Petrova, V. I.; Ivanov, G. I. *Environ. Sci. Technol.* **1996**, *30*, 1310–1320.
- Baumard, P.; Budzinski, H.; Garrigues, P. *Environ. Toxicol. Chem.* **1998**, *17*, 765–776.
- Talmage, S. S. *Environmental and Human Safety of Major Surfactants. Alcohol Ethoxylates and Alkylphenol Ethoxylates*; The Soap and Detergent Association, Lewis Publishers: Boca Raton, FL, 1994.
- Iino, F.; Imagawa, T.; Takeuchi, M.; Sadakata, M. *Environ. Sci. Technol.* **1999**, *33*, 1038–1043.

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