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Trend and Sources of Dioxin Pollution in Tokyo Bay, Estimated Based on the Statistical Analyses of Congener Specific Data

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Abstract

On the basis of the congener-specific analysis of dioxins in a dated sediment core, surface sediment, and soil samples, the sources and mass balance of dioxins in Tokyo Bay basin, Japan, were estimated. The dioxins in the sediment core showed that their deposition in the bay increased rapidly during the 1960s, peaked in the early 1970s and then decreased gradually. Principal component analysis of the congener-specific data showed that three major sources existed: combustion, pentachlorophenol (PCP), and chloronitrophen (CNP). PCP and CNP are paddy field herbicides used extensively in Japan in the past. The time trends of source contributions were estimated by multiple regression analysis using the source congener profiles. The results revealed that dioxin emission from PCP and CNP herbicides was high in the 1960s and the early 1970s, respectively. The mass balance of dioxins in the basin during the past 45 years showed that only a few percent of total dioxin load from agrochemicals were transported to the bay and accumulated in sediment, indicating that large part of dioxins was still remaining in terrestrial soil and river sediment of the basin and running off gradually.

1. Introduction

Although monitoring of environmental pollutants has been conducted by a variety of government and research organizations, the obtained data has not always been made much use of for the identification of sources and behaviors of the monitored pollutants. In this study, congener specific analyses of polychlorinated dibenzo-*p*-dioxin ands (PCDDs) and polychlorinated dibenzofurans (PCDFs) were conducted. And statistical analyses were applied to the obtained data. The methods proposed in this study succeeded in estimating the contributions of different dioxin sources to the sediment pollution in Tokyo Bay and their time trends.

2. Materials and Methods

We conducted comprehensive monitoring of dioxins in the Kanto region, Japan. The samples included air, atmospheric deposition, soil, aquatic sediment, and sediment core. Detailed congener-specific analysis of tetra- to octachlorinated dioxins was conducted using both DB-5 (5%-phenyl-methylpolysiloxane, J&W Scientific) and DB-17 (50%-phenyl-methylpolysiloxane, J&W Scientific) columns on HRGC/HRMS (Micromass Autospec-Ultima coupled with Hewlett-Packard HP6890GC) following conventional pretreatment procedures. The analytical procedures and the obtained data have been presented elsewhere [1-4]. Statistical analyses, principal component analysis and multiple regression analysis, were applied to the data using a software package (STATISTICA 2000

for Windows Release 5.5A, StatSoft, Inc., Tulsa, OK, USA) on a personal computer.

3. Results and Discussion

3.1. Principal component analysis

Principal component analysis (PCA) of dioxin concentration data (a total of 23 samples (seven surface sediments and 13 slices of a sediment core from Tokyo Bay, and three soil samples) with 82 individual or groups of congeners) was performed using a software package. The result showed that three major principal components (PCs) and two minor ones were extracted with an eigenvalue larger than 1 (Table 1). The three major PCs could be interpreted as dioxins from combustion [2], pentachlorophenol (PCP) [5] and chloronitrophen (CNP) [5], based on the characteristic dioxin congeners having high factor loadings in each PC. PCP and CNP were used extensively as rice field herbicides in Japan in the past. These three components accounted for over 93% of the total contribution. Thus, the two minor PCs are not considered to be significant.

Table 1 Results of principal component analysis (after varimax rotation*)

Principal components**	Contribution	Cumulative contribution	Characteristic congener*** (Factor loading > 0.7)	Interpretation
PC1	0.50	0.50	Most of TeCDFs, half of PeCDDs, most of PeCDFs, some HxCDDs, and most of HxCDFs.	Combustion
PC2	0.25	0.75	Most of HxCDDs, some HxCDFs, HpCDDs, most of HpCDFs, OCDD, and OCDF.	PCP
PC3	0.18	0.93	Some TeCDDs and PeCDDs, especially 1,3,6,8- & 1,3,7,9-substituted TeCDDs and PeCDDs, and 2,4,6,8-TeCDF.	CNP
PC4	0.021	0.95	(1,2,4,7,9-, 1,2,3,4,9- and 1,2,3,8,9-PeCDFs)****	Difficult
PC5	0.016	0.98	(1,2,8,9-TeCDF)****	Difficult

* Normalized varimax rotation was used. ** Principal components with eigenvalue > 1 were extracted.

*** TeCDD = tetrachlorodibenzo-*p*-dioxin, PeCDD = pentachlorodibenzo-*p*-dioxin, HxCDD = hexachlorodibenzo-*p*-dioxin, HpCDD = heptachlorodibenzo-*p*-dioxin, OCDD = octachlorodibenzo-*p*-dioxin, TeCDF = tetrachlorodibenzofuran, PeCDF = pentachlorodibenzofuran, HxCDF = hexachlorodibenzofuran, HpCDF = heptachlorodibenzofuran, OCDF = octachloro-dibenzofuran. **** Factor loadings were lower than 0.7 but higher than 0.3.

3.2. Estimation of source contributions by multiple regression analysis

Source contributions was be calculated by multiple regression analysis (MRA) using dioxin congener compositions of the sources as explanatory variables and those observed in environmental samples as criterion variables. The source dioxin compositions for combustion, PCP and CNP were adapted from atmospheric deposition in Yokohama [2] and impurities in PCP [5] and CNP [5] reported in literatures, respectively. In this study, MRA was performed for each homologue and then a summation of the results was made because some high-concentration congeners (for example, OCDD) greatly influenced the results. This method had an additional merit in that it could avoid the influence of homologue composition change across environmental media due to the difference of physical properties among

homologues. In the present calculation, as there were three major sources, more than four cases (isomers) were necessary to perform MRA. HpCDDs had two isomers and OCDD had only one isomer. Thus, HxCDDs, HpCDDs and OCDD were combined into one group. Similarly, HpCDFs and OCDF were combined. The obtained results for the sediment core samples are shown in **Figure 1**.

The concentrations of PCP- and CNP-originating dioxins in the sediment core peaked during the mid 1960s and beginning of the 1970s, respectively. On the other hand, combustion-originating dioxin was estimated to have increased during the 1960s, reached a plateau at the beginning of 1970s and then leveled off. The contribution of combustion in terms of toxic equivalent (TEQ) was greater than that in terms of amount.

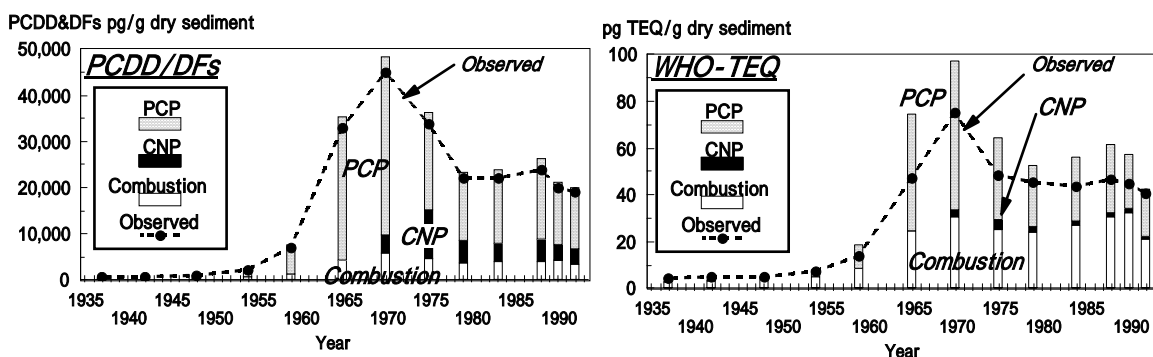


Figure 1 Estimated dioxin source contributions in Tokyo Bay sediment core in terms of total amounts [left] and toxic equivalents (TEQ) [right]

3.3. Dioxin mass balance in Tokyo Bay basin during the past 45 years

The dioxin load to the Tokyo Bay basin was estimated from the annual amounts of agrochemical shipment to Tokyo, Saitama, Chiba and Kanagawa Prefectures (Ministry of Agriculture, Forestry and Fishery, 1959-1996), the percentage of prefecture area belonging to the basin, and the dioxin content in the agrochemicals. The representative dioxin content in PCP (3,300 μg PCDD/DFs/g and 1.50 μg WHO-TEQ/g active ingredient) was determined by taking the arithmetic average of relevant data reported for Japanese agrochemicals [5, 6]. In the case of CNP, dioxin content dropped in 1982 due to the change of production process, thus two arithmetic averages were used for pre- and post-1982-periods (6000 μg PCDD/DFs/g and 3.60 μg WHO-TEQ/g active gradient for pre-1982; 710 μg PCDD/DFs/g and 0.022 μg WHO-TEQ/g active gradient for post-1982) [5, 6, 7, 8, 9].

The total loads of dioxins to the Tokyo Bay basin during the past 45 years from PCP were estimated to be 31,000 kg PCDD/DFs and 14 kg TEQ. Those from CNP were 9,300 kg PCDD/DFs and 5 kg TEQ. Assuming that annual dioxin deposition from combustion sources did not vary much during the past 45 years, the estimated recent average deposition in the Kanto region [2] was used as the average deposition of past years. The total dioxin loads to the basin from the three sources during the past 45 years (1951-1995) are listed in **Table 2**. On the other hand, the total amount of dioxin that sedimented in Tokyo Bay during the same periods was estimated from the sediment core data with horizontal corrections based on surface sediment data. The results are summarized in **Table 2**.

The results showed that only a small portion of dioxins sprayed to paddy field as agrochemical impurity have been deposited in the Tokyo Bay sediment, indicating that large part of the dioxin still exists

in the terrestrial soil or in the river sediment and will continue to run off into the Tokyo Bay.

Table 2 Mass balance of dioxins in Tokyo Bay basin between 1951 and 1995

Source	PCDD/DFs			WHO-TEQ		
	Load to basin (kg)	Amount existed in sediment (kg)	Run-off rate (%)	Load to basin (g TEQ)	Amount existed in sediment (g TEQ)	Run-off rate (%)
PCP	31,000	760	2.5	14,000	1,200	8.6
CNP	9,300	140	1.5	5,000	65	1.3
Combustion	42* 340**	150	39 (32)***	460* 3,600**	950	23 (14)***

* Direct deposition to seawater surface in Tokyo Bay. ** Deposition to terrestrial basin.

*** Run-off rate for load to terrestrial basin.

4. Acknowledgement

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Biographical Sketch

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Dr. Shigeki Masunaga received his bachelor degree in 1975 and received doctorate in urban engineering at the University of Tokyo in 1980. He worked as a research scientist at National Research Institute for Pollution and Resources, Agency of Industrial Science and Technology during 1980 and 1990. He stayed at the Environmental Research Laboratory, U.S. Environmental Protection Agency in Athens, GA from 1990 to 1991 as a senior research associate of National Research Council and conducted research on the degradation mechanism and rates of aromatic compounds in river sediments. He returned to National Institute of Resources and Environment, Agency of Industrial Science and Technology in 1991 and studied about the partitioning and degradation of environmental contaminants in aquatic environment from 1991 to 1996. He received Hirose Thesis Award from the Japan Society on Water Environment and the Second Environmental Chemistry Thesis Award, from Japan Society for Environmental Chemistry based on his studies on the behavior of organochlorine compounds in 1992 and 1995, respectively.

He moved to the Institute of Environmental Science and Technology, Yokohama National University as an associate professor in 1996 and was promoted to a professor in 1997. Due to the institutional change, he became a professor of Graduate School of Environment and Information Sciences, Yokohama National University in 2001. After his relocation to the university, his study was focused on the source and behavior analysis of dioxins in Japanese environment. He has succeeded in identifying dioxin sources in Japanese environment by detailed congener specific monitoring and statistical analysis of the obtained data.

He is currently studying environmental behavior of persistent organic pollutants (POPs) and other emerging pollutants, source analysis methods, and risk assessment and management of chemicals.