Historical Trends of Dioxin Sources to the Sediment Pollution in Tokyo Bay, Japan

Shigeki Masunaga [1], Yuan Yao [1], Takeo Sakurai [2], and Junko Nakanishi [3]
[1] Graduate School of Environment and Information Sciences
Yokohama National University
Yokohama, 240-8501, JAPAN
masunaga@ynu.ac.jp
[2] National Institute for Environmental Studies
Tsukuba, 305-8506, JAPAN
[3] Research Center for Chemical Risk Management
National Institute of Advanced Industrial Science and Technology
Tsukuba, 305-8569, JAPAN

1. Introduction

Although monitoring of environmental pollutants has been conducted by a variety of government and research organizations, the obtained data have 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 were proved to be successful 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-mehtylpolysiloxane, 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 (Sakurai et al., 2000; Ogura et al., 2001; Ogura et al., 2001; Yao et al., 2002).   Statistical analyses, namely 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. Identification of major sources by 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 (Ogura et al., 2001), pentachlorophenol (PCP) (Masunaga et al., 2001) and chloronitrophen (CNP) (Masunaga et al., 2001), 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 (Ogura et al., 2001) and impurities in PCP (Masunaga et al., 2001) and CNP (Masunaga et al., 2001) 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 dioxin amount.
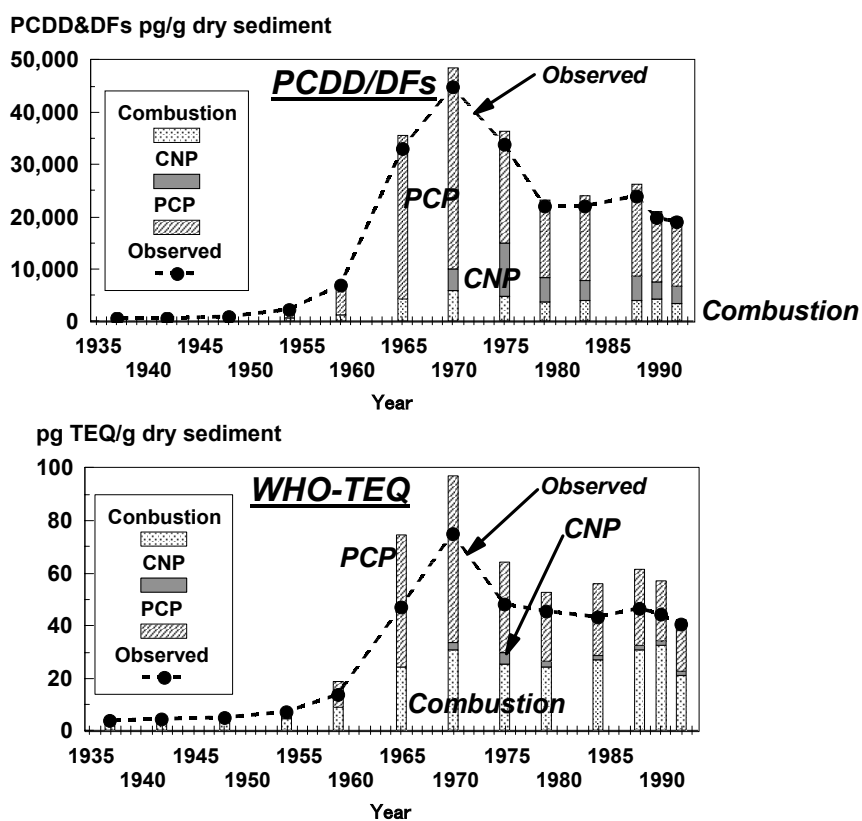

Figure 1   Estimated dioxin source contributions in Tokyo Bay sediment core in terms of total amounts [upper] and toxic equivalents (TEQ) [lower]

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 (Masunaga et al., 2001; Seike et al., 2003). 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 ingredient for pre-1982; 710 μg PCDD/DFs/g and 0.022 μg WHO-TEQ/g active ingredient for post-1982) (Masunaga et al., 2001; Seike et al., 2003; Yamagishi et al., 1981; Morita, 1991; Mitsui Chemicals, 2002).

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 average deposition in the Kanto region before introduction of intensive incineration source emission reduction measures (Ogura et al., 2001) 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.

References

Sakurai, T., Kim, J-G., Suzuki, N., Matsuo, T., Li, D-Q., Yao, Y., Masunaga, S., and Nakanishi, J.,2000. Polychlorinated dibenzo-p-dioxins and dibenzofurans in sediment, soil, fish, shellfish, and crab samples from Tokyo Bay area, Japan. *Chemosphere* 40, 627-640.

Ogura, I., Masunaga, S., and Nakanishi, J., 2001. Atmospheric deposition of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and dioxin-like polychlorinated biphenyls in the Kanto Region, Japan. *Chemosphere* 44, 1473-1487.

Ogura, I., Masunaga, S., and Nakanishi, J., 2001. Congener-specific characterization of PCDDs/PCDFs in atmospheric deposition: Comparison of profiles between deposition, source and environmental sink. *Chemosphere* 45, 173-183.

Yao, Y., Masunaga, S., Takada, H., and Nakanishi J., 2002. Identification of polychlorinated dibenzo-p-dioxin, dibenzofuran, and coplanar polychlorinated biphenyl sources in Tokyo Bay, Japan. *Environmental Toxicology and Chemistry* 21**,** 991-998.

Masunaga, S., Takasuga, T., and Nakanishi, J., 2001. Dioxin and dioxin-like PCB impurities in some Japanese agrochemical formulations. *Chemosphere* 44, 873-885.

Ministry of Agriculture, Forestry and Fishery, 1959-1996. Nouyaku Youran (Digest of Agrochemicals), Japan Plant Protection Association. (*in Japanese*)

Seike, N., Otani, T., Ueji, M., Takasuga, T., and Tsuzuki, N. 2003. Temporal change of polychlorinated dibenzo-*p*-dioxins, dibenzofurans and dioxin like polychlorinated biphenyls source in paddy soils. *Journal of Environmental Chemistry* 13, 117-131. (*in Japanese*)

Yamagishi, T., Miyazaki, T., Akiyama, K., Morita, M., Nakagawa, J., Hori, S., and Kaneko, S. 1981. Polychlorinated dibenzo-p-dioxins and dibenzofurans in commercial diphenyl ether herbicides, and in freshwater fish collected from the application area *Chemosphere* 10, 1137-1144.

Morita, M., 1991. Dioxin concentration in agrochemicals. *in* Japan Food Research Laboratories. FY1990 Report on the examination method of safety of agrochemical impurities, 96-107. (*in Japanese*)

Mitsui Chemicals, 2002. Analytical results of dioxins in herbicide CNP, http://www.mitsui-chem.co.jp/whats/020412a.pdf (2002.4.12). (*in Japanese*)