Source and Behavior Analyses of Dioxins Based on Composition Data

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Abstract

As a case study of chemical risk assessment, dioxin was studied from a wide perspective. In this paper, the atmospheric behavior of dioxins from emission to deposition and a source identification method using a combination of principal component analysis and multiple regression analysis are discussed. Based on these results, the mass balances of dioxin in the Tokyo Bay basin for the past 45 years are estimated.

1. Introduction

As an important case study of the risk evaluation and management of chemicals, the dioxin problem was studied extensively in this project. A wide range of studies, including source and behavior analyses based on monitoring, exposure assessment, human health and ecological risk assessment, and a cost effectiveness analysis of emission reduction measures, have been performed. In this presentation, I will focus on the findings of the source and behavior studies. Other aspects of the studies will be presented in this workshop by Kikuo Yoshida, Masanao Iseki, Mariko Murata and Mitsuo Kishimoto.

Dioxin emission reduction measures against municipal solid incinerators were strengthened by the Japanese government in 1997 without an understanding of the actual situation and causes dioxin pollution. In this project, we attempted to provide a scientific basis for better decision making on dioxin problems. We performed detailed environmental monitoring by quantifying over 80 peaks in the GC/MS chromatograph which correspond to individual or groups of tetra- to octa-chlorinated dibenzo-*p*-dioxin and dibenzofuran congeners. We also provided basic information on dioxin pollution in Japan based on a statistical analysis of the congener-specific data. Here, applied statistical methods and some of the highlights of the results will be discussed.

2. Behavior of dioxins in the atmosphere

The current major source of dioxins is considered to be the combustion process (Environment Agency, 2000). Understanding the atmospheric behavior of dioxins is important for the prediction of the effectiveness of emission control measures for combustion. Thus, in this project, dioxins in air, atmospheric deposition, and combustion sources in the Kanto region, Japan, were studied (Ogura *et al*., 2001a; Ogura *et al*., 2001b).

2.1 *Dioxin congener composition in emission source and environment*

The study of dioxin compositions in combustion sources (flue gas), air, atmospheric deposition, and soil which has received dioxins exclusively from atmospheric deposition showed that their isomer compositions were quite similar while their homologue compositions were different. In addition, the isomer compositions in air and atmosphere did not vary between monitoring sites and between seasons in Kanto region. Some of the isomer compositions in combustion sources were similar to those in air and atmospheric deposition, but others were somewhat different. These observations indicated that dioxin isomer compositions in air are reasonably uniform both area-wide and for all seasons. This may be due to the through mixing of various emission sources and/or the degradation process in the atmosphere. On the other hand, differences in homologue compositions between media indicated that their atmospheric behaviors were different. It is concluded that while isomer composition remains the same between environmental media due to similarities in their molecular physical properties, homologue composition changes due to differences in their physical properties.

2.2 *Difference in gas-particulate phase partition among homologues*

Dioxins in air exist either as gas phase or particulate phase and the two phases behave differently. The partition process was studied by determining the two phases individually. The partition depends on the temperature, as shown in Figure 1. About half of the tetrachlorinated dibenzofurans (TeCDFs) existed as gas phase at a temperature of 5ºC, whereas hepta- and octachlorinated dibenzofurans (HpCDFs & OCDF) existed almost entirely as particulate phase under 30ºC. The partition of penta- and hexachlorinated dibenzofurans (PeCDFs & HxCDFs) depends strongly on temperature. These differences in partition influence the rate of the atmospheric deposition process.

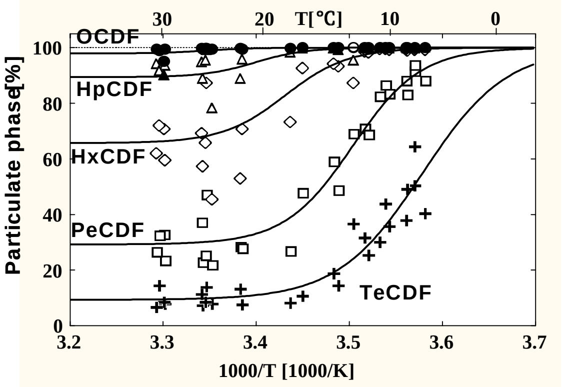
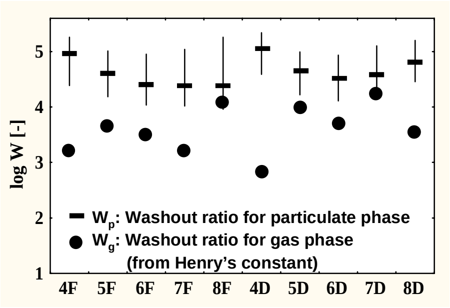


Figure 1. **Temperature dependence of gas and particulate phase partition (PCDFs)**
(Revised. See slide)

2.3 *Difference in atmospheric deposition among homologues*

Chemicals in air deposit to a soil or water surface by two mechanisms, wet deposition and dry deposition. In wet deposition, rain washes out the gas and particulate phase chemicals. In dry deposition, gas phase chemicals diffuse to dissolve into a soil surface and particulate phase chemicals fall to the ground with gravity. In this project, the determinations of dioxins in rain and in dry deposition were conducted concurrently with that in air. Subsequently, both washout ratios and dry deposition rates for the gas and particulate phases were estimated (Figure 2). The obtained washout ratios and dry deposition rates were higher for particulate phase than for gas phase dioxins. The difference in ratio and rates among homologues was explained by the difference in particulate diameter distribution among homologues.



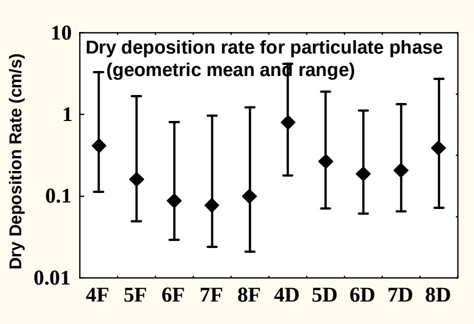


Figure 2-a Washout ratios for gas phase and particulate phase dioxins (Revised. See slide)
Figure 2-b Dry deposition rates for particulate phase dioxins

2.4 *Difference in atmospheric fate among homologues*

The atmospheric fates of dioxin homologues were simulated using a simple box-type model representing the Kanto region and the combustion sources. Examples of simulated results are shown in Figure 3. Although the results depended on environmental conditions such as the wind speed and mixing zone height, some important trends can be observed. First, the rates of elimination from air depended on the homologues. Second, the rate also depended on temperature for each homologue. These changes were explained by the difference between gas and particulate phase partition.

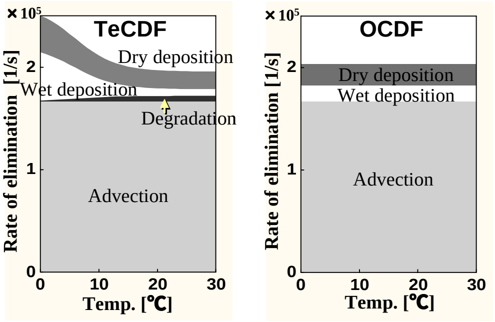


Figure 3. Estimated atmospheric fate of dioxins emitted from combustion sources

Model calculation was conducted by simulating the Kanto region as a 180 km x 180 km x 400 m box with average climate parameters.

2.5 *Isomer composition as a key for source identification*

As discussed above, isomers that have relatively similar physical characteristics are transported similarly in environmental media. On the other hand, homologues have different physical properties and moves differently in environmental media. Thus, isomer composition should be used as a basis of source identification. It should be noted, however, that isomer composition may also change when biological processes are involved.

3. Source identification

The source identification of current dioxin pollution was attempted in this project and satisfactory results were obtained. This success was mainly due to the detailed analysis of dioxin congeners. 2,3,7,8-Chlorine substituted congeners are not sufficient for the purpose of source identification. Here, the relationship between the level of dioxin congener information and the success of principal component analysis (PCA) as a means of source identification is discussed. Data used for the example are congener-specific dioxin data of surface sediments and a sediment core from Tokyo Bay and some soil samples (total of 23 samples) (Sakurai, *et al.*, 2000; Yao *et al*., 2000).

3.1 *Principal component analysis with different levels of dioxin information*

1) All congeners

Principal component analysis of dioxin congener-specific data (23 samples with 82 individual or groups of congeners) was performed using a software package (STATISTICA 2000 for Windows Release 5.5A, StatSoft, Inc., Tulsa, OK, USA). The result showed that three major components and two minor ones were extracted with an eigenvalue larger than 1 (Table 1). The three major components could be interpreted as dioxins from combustion, pentachlorophenol (PCP) and chloronitrophen (CNP), respectively. PCP and CNP have been used extensively as rice field herbicides. These three components accounted for over 90% of the total contribution.

Table 1 Results of principal component analysis with different level of dioxin information (after varimax rotation)

Principal components*	Contribution	Cumulative contribution	Characteristic congeners (factor loadings > 0.7)	Interpretation
All congeners				
PC1	0.50	0.50	most of TeCDFs、 half of PeCDDs, most of PeCDFs, some of HxCDDs, most of HxCDFs	Combustion
PC2	0.25	0.75	most of HxCDDs, some of HxCDF, HpCDDs, most of HpCDFs, OCDD, OCDF	PCP
PC3	0.18	0.93	some of TeCDDs and PeCDDs, especially 1368- & 1379-substituted TeCDDs and PeCDDs, 2468-TeCDF	CNP
PC4	0.021	0.95	(12479-, 12349- & 12389-PeCDFs)**	Impossible
PC5	0.016	0.98	(1289-TeCDF)**	Impossible
2378-congeners only				
PC1	0.50	0.50	HxCDDs, HpCDD, OCDD, 2378-TeCDF, 123478-HxCDF, HpCDF, OCDF	Impossible
PC2	0.46	0.96	2378-TeCDD, 12378-PeCDD, PeCDFs, 123678-/234678-/123789-HxCDF	Impossible
2378-congeners+ non-2378-homologues				
PC1	0.45	0.45	OCDD, OCDF, HpCDDs, HpCDFs, some of HxCDDs & HxCDFs	PCP
PC2	0.40	0.85	most of TeCDFs, PeCDFs and HxCDFs	Combustion
PC3	0.11	0.96	non-2378-TeCDDs, non-2378-PeCDDs	CNP
2378-congeners + some TeCDDs and TeCDFs, residual homologues				
PC1	0.41	0.41	OCDD, OCDF, HpCDDs, HpCDFs, some of HxCDDs & HxCDFs	PCP
PC2	0.38	0.79	most of TeCDFs, PeCDFs, and HxCDFs	Combustion
PC3	0.18	0.96	1368-/1379-TeCDDs, residual-TeCDDs, residual-PeCDDs	CNP

* Principal components with eigenvalue > 1 were extracted.
** Factor loadings were less than 0.7, but higher than 0.3.

2) 2,3,7,8-Chlorine substituted congeners only

2,3,7,8-Chlorine substituted congeners (2378-congeners) were selected from the above data set and PCA was performed (23 samples with 17 congeners). Two components were extracted, one with higher chlorinated 2378-congeners and one with lower chlorinated ones (Table 1). However, interpretation of the components was impossible. Plotting the 2378-congeners in the PCA plot obtained using all congener data showed that there are 2378-congeners with factor loadings higher than 0.8 for PC1 (combustion) and PC2 (PCP) (Figure 4). However, for PC3

(CNP), there were no 2378-congeners with factor loadings higher than 0.6 (Figure 4). Thus, 2378-congener data alone are not sufficient to identify CNP as a major component.

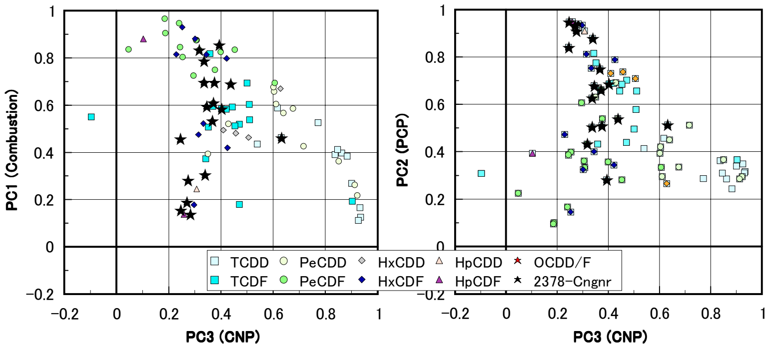


Figure 4 Factor loading plot of PCA result with all congener data

2378-congeners are highlighted with star marks.

3) 2,3,7,8-Chlorine substituted congeners and homologues

Very often, 2378-congeners and homologue composition data are available. In order to make the variables independent, the 2378-congener concentrations were subtracted from their corresponding homologue concentrations and non-2378-homologue concentrations were obtained. Then, PCA was performed using this data set (23 samples with 25 variables). The result is shown in Table 1. In this case, three major components were extracted and could be interpreted as combustion, PCP and CNP sources. Non-2378-TeCDDs and non-2378-PeCDDs had high factor loadings for CP3 (CNP). This indicates that the addition of homologue composition for PCA analysis is effective when only these three sources are concerned. However, its effectiveness is limited when other dioxin sources are present. No minor component with an eigenvalue larger than 1 was extracted in this analysis while two minor components were extracted in the PCA with all congener information.

4) 2378-congeners, 1368- & 1379-TeCDD, 1368- & 1278-TeCDF, and homologues

Recently, some of the relatively major dioxin congeners in the environmental samples have been quantified in addition to the 2378-congeners. Among these are 1368- and 1379-TeCDDs and 1368- and 1278-TeCDFs. Will the addition of these congeners improve the PCA result (23 samples with 29 variables)? The obtained result is almost the same as that from 2378-congeners and homologues (Table 1). 1379- and 1379-TeCDDs were correlated to the CNP source and 1368- and 1278-TeCDFs were correlated to the combustion source. Thus, although the addition of these congener data may improve the reliability of PCA, it may not help to identify a new component.

3.2 *Estimating the contribution of sources by multiple regression analysis*

When performing PCA, congener-specific data are transformed to a correlation matrix, and the calculated contribution of each PC does not correspond to a real dioxin concentration. In addition, factor scores do not correspond to a real dioxin concentration, either. Thus, an understanding of contributions from different dioxin sources in terms of real dioxin concentration cannot be gained from PCA. Multiple regression analysis (MRA) can be used to fill this gap. In MRA, dioxin source compositions are required as independent variables and those in samples are regarded as dependent variables.

In the previous workshop, MRA was performed with the input of all congener data at once. However, a problem was noted as the obtained result depended heavily on source profiles. In particular, dioxin congener profiles in agrochemicals varied so significantly among formulations that obtaining a reliable average source profile was difficult. In the case of PCP, the concentration of OCDD was much higher than other congeners and varied; however, the isomer compositions within each homologue were relatively stable. Thus, in this study, MRA calculations were performed for each homologue and then summed up. This method has additional merit in that it can avoid the influence of homologue composition change across environmental media. In the present calculation, as there were three major sources, more than four cases (isomers) were necessary. Thus, HxCDDs, HpCDDs and OCDD were combined. Similarly, HpCDFs and OCDF were combined. MRA for each homologue seemed to yield better results.

4. Dioxin mass balance in the Tokyo Bay basin (update)

With the new analysis method discussed above and additional data, the updated dioxin mass balance in Tokyo Bay basin was estimated. Additional data obtained after the previous report (Masunaga, 1998) included dioxin concentrations in Japanese agrochemicals (Masunaga and Nakanishi, 1999) and those in dated sediment core (Sanada et al., 1999; Yao et al., 2000) from Tokyo Bay.

4.1 *Sources of dioxins in Tokyo Bay sediment*

The major sources of dioxin in Tokyo Bay sediment were shown to be combustion, PCP and CNP as discussed above. The contributions of these sources estimated using MRA are shown in Figure 5. The estimated dioxin input to the basin and the concentration in the slices of dated sediment core are shown in Figure 6. These results show that dioxin input to the basin was substantial during the 1960s and 1970s. A corresponding increase in pollution in sediment from these sources was also observed. However, after the rapid decrease of input, the decrease of pollution in sediment was less conspicuous. This indicates that dioxins accumulated in agricultural fields continued to run off through river systems and contaminate the coastal environment. This is an important observation because Japanese people takes in dioxins mainly through fish and shellfish consumption.

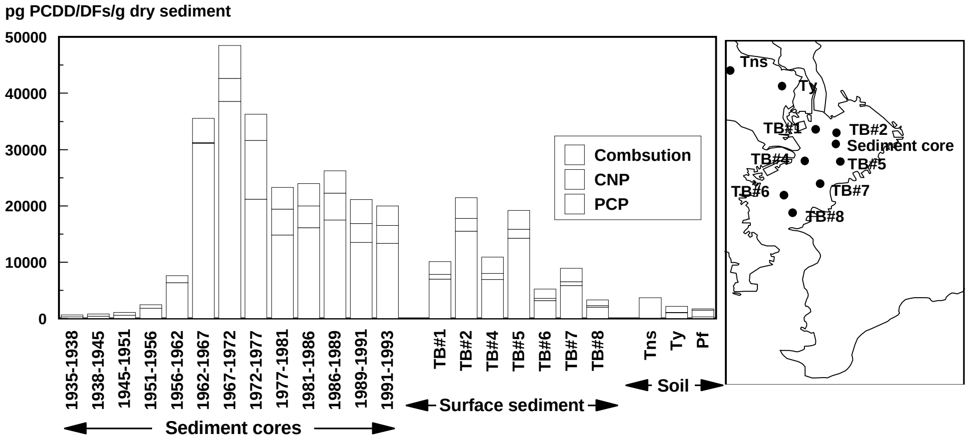


Figure 5 Sources of dioxins in surface sediment and sediment core from Tokyo Bay
Map shows the location of sampling sites.

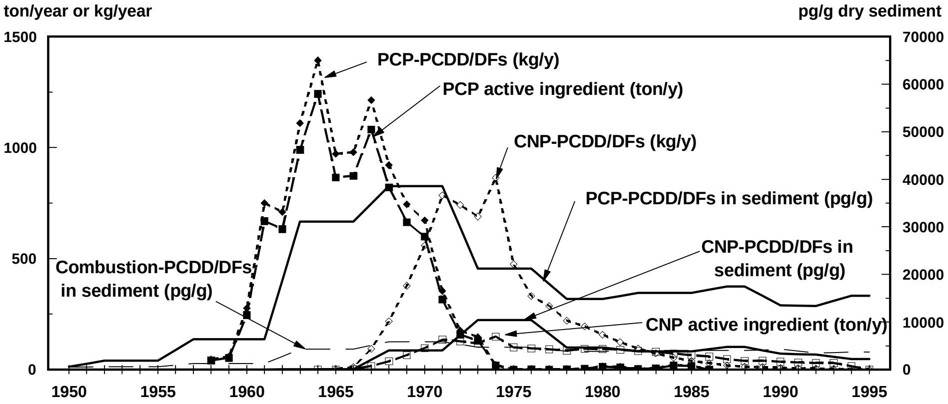


Figure 6 Trend of dioxin input to the Tokyo Bay basin from agrochemical use and dioxin concentration in dated Tokyo Bay sediment core.

4.2 *Dioxin mass balance in the Tokyo Bay basin*

The amount agrochemical use in the Tokyo Bay basin was estimated from the agrochemical shipment data to Tokyo, Saitama, Chiba and Kanagawa prefectures (Noyaku-Yoran, 1959-1996) with corrections based on the Tokyo Bay catchment area. As a dioxin concentration in PCP, an average of dioxin contents reported worldwide was used (1,120 µg PCDD/DFs/g and 1.25 µg WHO-TEQ/g active ingredient). For CNP, dioxin content was assumed to have decreased yearly based on the 5 samples analyzed in this project. The calculated load is shown in Figure 6. Assuming that annual dioxin deposition from the combustion sources did not vary during the past 45 years (Figure 6), an estimated recent deposition in the Kanto region (Ogura *et al.*, 2001a) was used as an average 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 sedimented in Tokyo Bay during the past 45 years was estimated from the core data with horizontal corrections based on surface sediment data. The result is summarized in Table 2. The revised mass balance differs from the previous one on the following points:

a) An unknown factor that was significant in the Kasumigaura Lake basin and less in the Tokyo Bay basin, was absent because the data from the Kaumigaura basin were not included in the present analysis.

b) Both input and sedimented amounts of dioxin from PCP increased and the run-off ratio remained the same.

c) Amounts of sedimented dioxin from CNP and combustion increased.

d) The mass balance calculation in terms of TEQ became possible due to the availability of 2378-congener concentrations in CNP.

The run-off ratio for PCP was larger than that for CNP, which is reasonable because PCP was used prior to CNP. The run-off ratios for PCDD/DFs and TEQ should be similar but were four times different in the case of CNP . This may be due to error in the average dioxin content estimation in agrochemical formulations, which is very difficult because of a wide range of variation depending on the formulations. The run-off ratio for combustion was rather high probably because large parts of combustion dioxins were brought into the basin as wet deposition.

Table 2 Dioxin mass balances in Tokyo Bay basin during the past 45 years (1951-1955)

	PCDD/DFs			WHO- TEQ		
Sources	Input to basin (kg)	Accumulation in sediment (kg)	Run-off ratio (%)	Input to basin (g TEQ)	Accumulation in sediment (g TEQ)	Run-off ratio (%)
PCP	11,000	760	7.2	12,000	1,200	10
CNP	6,500	140	2.2	10,000	65	0.63
Combustion	42*	150	40	460*	950	23
	340#		(33)**	3,600#		(14)**

* Input directly to water surface of Tokyo Bay. # Input to terrestrial surface in Tokyo Bay basin.
** Run-off ratio for terrestrial input.

5. Conclusions

In this project, the study of environmental behaviors, source identification and mass balances of dioxins in some Japanese water bodies were successfully carried out in this project based on the detailed dioxin congener-specific data. The following are some of the important results.

a) A source identification method based on congener-specific data was developed and agrochemical use was found to be a significant source of current dioxin pollution in Japan.

b) Information on the dioxin contents of some old Japanese agrochemicals was obtained and time trends of dioxin emission from these sources were estimated.

c) Mechanisms of environmental behavior of dioxins such as gas-particulate partition and atmospheric deposition were elucidated.

d) The dioxin mass balances in the Tokyo Bay and Lake Shinji basins over the past several decades were obtained.

The above results provide basic information for current assessment, the future prediction of human exposure, and effectiveness evaluation of emission reduction measures.

6. Acknowledgement

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