ENVIRONMENTAL LEVELS I

QUANTITATIVE ESTIMATION OF DIOXIN SOURCES ON THE BASIS OF CONGENER-SPECIFIC INFORMATION

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Introduction

Identification of source is very important for taking better countermeasures against dioxin pollution. Seventeen 2,3,7,8-chlorine-substituted PCDD and PCDF congeners and ten PCDD and PCDF homologues are monitored in the ordinary dioxin analysis. Such information, however, is often not enough for source identification. To cope with this problem, we have been analyzing all the tetra- to octa-chlorinated PCDD/DF congeners. In this paper, the source identification powers of different levels of dioxin monitoring information are compared. Also the method for estimating contributions from different sources to the dioxin pollution is proposed.

Materials and Methods

We did comprehensive monitoring of dioxins in the Kanto area, Japan where metropolitan Tokyo is located. The analyzed environmental media included air, atmospheric deposition, surface sediment, sediment core and soil samples. The detailed congener specific analyses of tetra- to ocata-chlorinated dioxins were performed using both DB-5 and DB-17 columns (J&W Scientific) on HRGC/HRMS (Micromass Autospec-Ultima) following ordinary pretreatment procedures. The obtained data have been presented elsewhere [1, 2, 3, 4]. The statistical analyses of the data were performed using a software package (Statistica 2000, Rel. 5.5A, StatSoft, Inc.).

Results and Discussions
Behaviors of dioxins in the environment: Homologue and isomer composition

Dioxin homologue compositions in the air, atmospheric deposition and soil (which received dioxins only through atmospheric deposition) samples from the Kanto area were variable, depending on the environmental media and location. The isomer compositions within each homologue group, however, were quite stable across these media and location. This was probably because isomers, having similar physical characteristics, were transported similarly through environmental media. Thus, it was shown that isomer compositions should be used as a basis of source identification. It should be noted, however, that isomer composition changes when biological processes are involved.

Principal component analysis with different levels of dioxin information

Principal component analysis (PCA) has been often applied as a means of source identification.   Most studies used 2,3,7,8-congener or homologue compositions as input data, but rarely succeeded in the quantitative estimations of source contribution.   We examined how the detailed information of dioxin would influence the PCA results.   Congener-specific dioxin data of surface sediments and a sediment core from Tokyo Bay and some soil samples in the basin (total of 23 samples) [1, 2] were used as an example data set.

1) All congeners

Principal component analysis of dioxin congener-specific data (23 samples with 82 individual or group of tetra- to octa-chlorinated congeners) was performed.   Three major and two minor principal components (PCs) with an eigenvalue larger than 1 were extracted (Table 1).   The three major PCs were interpreted as dioxins originated from combustion, pentachlorophenol (PCP) and chloronitrophen (CNP), respectively.   PCP and CNP have been used extensively as rice field herbicides in Japan.   The major three PCs accounted for over 93% of the total contribution.

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

2,3,7,8-Chlorine substituted congeners (2,3,7,8-congeners) were selected from the above data set and PCA was performed (23 samples with 17 congeners).   Two PCs were extracted, one with highly chlorinated congeners and one with lowly chlorinated ones (Table 1).   Highlighting of the 2,3,7,8-congeners in the factor loadings plot obtained with all congener data set showed that there were 2,3,7,8-congeners with factor loadings higher than 0.8 for PC1 (combustion) and PC2 (PCP) (Figure 1).   However, for PC3 (CNP), only one 2,3,7,8-congener had factor loadings higher than 0.6 (Figure 1).   Thus, 2,3,7,8-congener data alone was shown to be not sufficient to identify CNP as a major component.

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

Homologue composition data are often available in addition to 2,3,7,8-congeners.   To make the variables independent, the 2,3,7,8-congener concentrations were subtracted from their corresponding homologue concentrations and non-2,3,7,8-homologue concentrations were obtained.   Then, PCA was performed using this data set (23 samples with 25 variables) (Table 1). In this case, three major PCs were extracted and could be interpreted as combustion, PCP and CNP sources.   Non-2,3,7,8-TeCDDs and non-2,3,7,8-PeCDDs had high factor loadings for PC3 (CNP). Thus, addition of homologue composition was shown to effective when these three
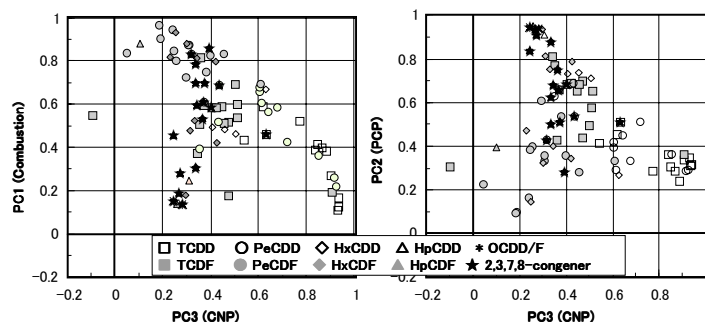

Figure 1. Factor loadings plot of PCA with all congener data
2,3,7,8-congeners are highlighted with star marks.

Table 1 Results of PCA 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, and most of HxCDFs.	Combustion
PC2	0.25	0.75	most of HxCDDs, some of HxCDF, HpCDDs, most of HpCDFs, OCDD, and OCDF.	PCP
PC3	0.18	0.93	some of TeCDDs and PeCDDs, especially 1368- & 1379-substituted TeCDDs and PeCDDs, and 2468-TeCDF.	CNP
PC4	0.021	0.95	(12479-, 12349- and 12389-PeCDFs)**	Difficult
PC5	0.016	0.98	(1289-TeCDF)**	Difficult
2,3,7,8-congeners only				
PC1	0.50	0.50	HxCDDs, HpCDD, OCDD, 2378-TeCDF, 123478-HxCDF, HpCDF, and OCDF.	Difficult
PC2	0.46	0.96	2378-TeCDD, 12378-PeCDD, PeCDFs, and 123678-/234678-/123789-HxCDF.	Difficult
2,3,7,8-congeners+ non-2,3,7,8-homologues				
PC1	0.45	0.45	OCDD, OCDF, HpCDDs, HpCDFs, and some of HxCDDs & HxCDFs.	PCP
PC2	0.40	0.85	most of TeCDFs, PeCDFs & HxCDFs.	Combustion
PC3	0.11	0.96	non-2378-TeCDDs, non-2378-PeCDDs.	CNP
2,3,7,8-congeners + some TeCDDs and TeCDFs, residual homologues				
PC1	0.41	0.41	OCDD, OCDF, HpCDDs, HpCDFs, and some of HxCDDs & HxCDFs.	PCP
PC2	0.38	0.79	most of TeCDFs, PeCDFs, & HxCDFs.	Combustion
PC3	0.18	0.96	1368-/1379-TeCDDs, residual-TeCDDs, and residual-PeCDDs.	CNP

* Extracted principal components with eigenvalue larger than 1.
** Factor loadings were less than 0.7, but higher than 0.3.

sources were concerned. Its effectiveness was doubtful when other dioxin sources were present because no minor PCs with an eigenvalue larger than 1 was extracted in this analysis.

4) 2,3,7,8-congeners, 1,3,6,8- & 1,3,7,9-TeCDD, 1,3,6,8- & 1,2,7,8-TeCDF, and homologues

Recently, a few more dioxin congeners such as 1,3,6,8-/1,3,7,9-TeCDDs and 1,3,6,8-/1,2,7,8-TeCDFs are also reported in addition to the 2,3,7,8-congeners. The obtained PCA result (23 samples with 29 variables) was almost the same as that from 2,3,7,8-congeners and homologues (Table 1). Although the addition of these congeners may improve the reliability of PCA, it may not help to identify a new component.

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 obtained 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.

When MRA was performed with the input of all congener data at once, the results depended heavily on dioxin source compositions. In particular, dioxin congener profiles in agrochemicals varied so significantly among formulations that it was very difficult to obtain a reliable average source profile. 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, MRA calculations were performed for individual homologues and then summed up. This method had additional merit in that it could 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. Figure 2 illustrates the results of source contribution in the dated Tokyo Bay sediment core estimated by the proposed method. The contributions from agrochemicals, namely PCP and CNP were large during the 1960s and 1970s.
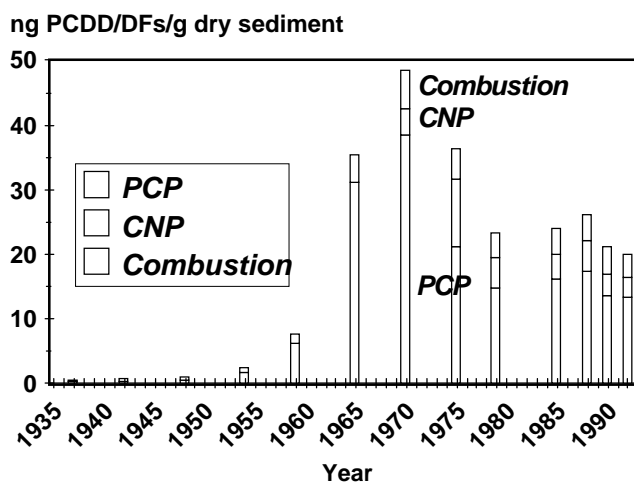

Figure 2. Sources of dioxins in the dated sediment core from Tokyo Bay

Conclusions

Combination of PCA and MRA is a powerful tool for the identification and apportioning of dioxin sources in contaminated environment. Dioxin data based on all the congeners are desirable for the success of this tool.

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