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Application of Principal Componen: Analysis to Isomer-specific Data Matrix of PCDDs and PCDFs

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Introduction

As a result of their lipophilic nature, polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) accumulate in organic matrices such as sediment, soil, and biota[1]. Loss of PCDD/Fs in sediment and soil is considered to be minimal[1]. Thus sediment and soil will work as conservative matrices which record the information of PCDD/F inputs.

Since PCDD/Fs are made up of 210 congeners, analysis of these compounds yields a considerable amount of data. Multivariate analyses have been utilized by many researchers to reduce the complexity of these data sets. Principal component analysis (PCA), the goal of which is the reduction of data dimensions and the interpretation of the data, have been applied successfully by several researchers to cluster the samples or to reveal the proximity between the source and environmental samples.

However, in most of these applications, only the homologue total values and/or concentrations of 2378-substituted compounds were used. The inclusion of other isomers as input variables may result in a more comprehensive analysis of the data matrix structure[2]. In addition, only a limited number of studies have resulted in principal components(PCs) that were clearly related to specific sources of PCDD/Fs[3, 4].

In this study, we applied PCA to the results of isomer-specific determination of PCDD/Fs in sediment and soil samples collected from Lake Kasumigaura, the second-largest lake in Japan, and its drainage area.

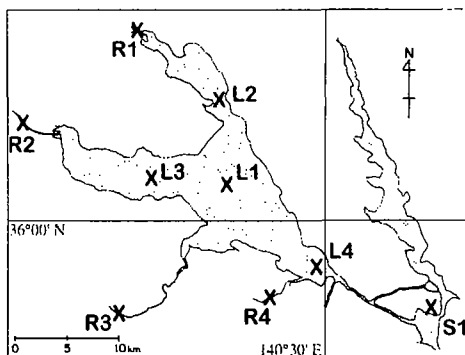## Materials and Methods

Determination of PCDD/Fs

The sampling points are shown in Figure 1. The sediment sampling points were selected to represent the spatial distribution of PCDD/Fs in this area.

The samples were analyzed following the procedure described previously[5]. Briefly, Soxhlet extracts were treated with concentrated sulfuric acid and copper, and then subjected to silica gel, alumina and

activated carbon column purification. The final eluate was isomer-specifically analyzed by high-resolution gas chromatography/high-resolution mass spectrometry equipped with a DB-5 (60m × 0.25 mm i.d., J&W Scientific) column. Chromatographic peaks were assigned according to the report by Ryan et al.[6]. The precision of the measurement was estimated to be below 20% for 95% of the chromatographic peaks with the median precision of 7.1%, according to the coefficients of variation of a triplicate analysis.

Principal component analysis

All the data values were log-transformed to improve the approximation to the normal distribution before PCA. Although the number of samples was limited, the distribution of log-transformed values around each mean value was

Figure 1: Lake Kasumigaura and the sampling points. Surface sediment was sampled at each lake (L1-L4) and river (R1-R4) sampling point in November 1994. Surface soil was sampled at a paddy field (S1) near the lake in July 1993.

symmetric, suggesting an acceptable level of normality. From 89 peaks of 4 to 8 chlorinated PCDD/Fs which separate on our DB-5 chromatogram, 73 peaks of reliable quantitation (i.e., without samples of N.D. or samples with significant interference) were subjected to PCA. Correlation matrix was used as the input to PCA. Before further discussion, the calculated eigenvectors were varimax-rotated to improve interpretability. Statistical analyses were carried out on VisualStat (STATISTICA Family) for Windows (StatSoft, USA).
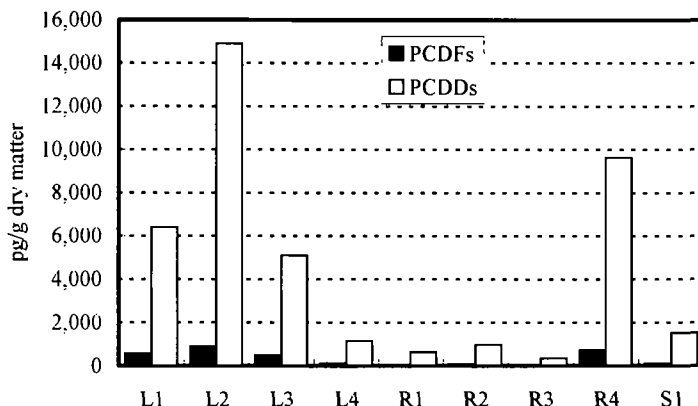
Results and Discussion

PCDD/F concentrations

The total PCDD and PCDF concentrations at each sampling point are shown in Figure 2. PCDDs comprise 90% to 95% of the total PCDD/F concentration in each sample. These PCDD/F

Figure 2: Total PCDD and PCDF concentrations at each sampling point

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Table 1: Description of calculated principal components (PCs)

PC	contribution (%)	isomers with high (>0.7) loading values	source estimation
1	39	most of the TCDF and PeCDF isomers	air
2	22	2468-TCDF, 1368-TCDD, 1379-TCDD, 1369-TCDD, 1237/1238-TCDD, 12368-PeCDD, 12379-PeCDD	CNP
3	22	124689-HxCDF, 1234689-HpCDF, OCDF, OCDD	PCP
4~	less than 0.6 % each		

concentrations are comparable to the reported values for the Japanese general environment[7].

Description of the principal components

After varimax rotation, PC-1, 2 and 3 accounted for 39%, 22% and 22% of the total standardized variance, respectively. Each of the other PCs accounted for less than 0.6%. Thus, the number of PCs were determined to be three. Description of the 3 major PCs is summarized in Table 1, and discussed in detail in the following sections.

Although PCDD/Fs are considered stable in sediment and soil, they may undergo selective enrichment or degradation of specific congeners during transportation. These potential changes were not taken into account in the following discussion.

PC-1

PC-1 has relatively high loading values (*r*≈0.7) for most of the TCDF and PeCDF isomers and some of the PeCDD and HxCDD isomers. Figure 3 shows TCDF and PeCDF isomer patterns of reconstructed Kasumigaura data and airborne PCDD/Fs reported by Eitzer and Hites[8]. Although the composition of airborne PCDD/F may change through the process of deposition[9], the similarity between the *Kasumigaura* and *airborne* isomeric patterns suggests that PC-1 represents the variance from airborne input of PCDD/Fs.

Many authors have reported background airborne PCDF profiles that are dominated by 4 and 5 chlorinated PCDFs (Ref. 8, for example). Atmospheric deposition has been considered as one of the major sources of PCDD/F input to sediment[10]. These two findings also support the conclusion that PC-1 represents the input from airborne PCDD/Fs.

PC-2

PC-2 has high loadings (>0.75) on a limited number of lower chlorinated compounds, namely, 2468-TCDF, 1368-TCDD, 1379-TCDD, 1369-TCDD, 1237/1238-TCDD, 12368-PeCDD, and 12379-PeCDD. Most other isomers have lower loadings (<0.50) compared to those. Yamagishi *et al.*[11] reported 1368-TCDD, 1379-TCDD and 2468-TCDF as the main components of PCDD/Fs in the herbicide CNP, resulting from chemical by-reaction of chlorophenols. Since all 8 aforementioned isomers appear structurally related, they can all be considered as impurities in CNP. Thus PC-2 is concluded to represent the variance by PCDD/Fs originating from the herbicide. In addition, 23468-PeCDF, which is structurally related to 2468-TCDF, shows a relatively high correlation (*r*≈0.7) with PC-2, which also supports this hypothesis.

More than 70,000 tons of CNP had been applied in Japan mainly to paddy fields until the practical ban of its use in 1994. CNP was reported to contain about 100 and 10 µg/(g formulation) of TCDDs and TCDFs, respectively[11]. Hiraoka estimated CNP to be one of the main sources of PCDD/Fs in the Japanese environment[12]. Paddy fields comprise more than 20% of the Lake Kasumigaura's catchment

area. Hence it is reasonable that CNP-derived PC accounts for a considerable part of the total variance.

PC-3

Loading values of PC-3 are highly correlated (r>0.70) with 124689-HxCDF, 1234689-HpCDF, OCDF, and OCDD and less correlated (r<0.50) with most of the 4 and 5 chlorinated compounds. This PC is interpreted to represent the variance by pentachlorophenol (PCP)-derived PCDD/Fs, because these 4 compounds were reported to be the main constituent of PCDD/Fs in PCP[13]. About 175,000 tons of PCP had been sold in Japan until its production decreased dramatically in 1971. It is not surprising that PCDD/Fs originating from PCP still remain in the environment, considering the persistence of these compounds.

PC scores

PC scores for each sample are shown in Table 2.

For PC-1, the lake sediment samples show high scores and the river sediment samples show low scores. Airborne dioxins will deposit to the lake and the rivers equally and be adsorbed to the sediment. River sediment will gradually be transported to the lake and accumulate there. This model may explain the difference in the PC-1 scores between lake samples and river samples.

The R4 (Shintone River) sample has the highest score for PC-2 and the paddy-field-soil sample the second highest. More than 50% of the land use around Shintone River is as paddy fields. It is thus reasonable that these 2 samples show high PC-2 scores, because the herbicide CNP had been applied mainly to paddy fields. The amount of CNP applied to each paddy field differs greatly depending on farming strategies. Paddy-field soil may drain out to receiving rivers and accumulate there. This difference in application and accumulation in sediment might explain the higher score for R4
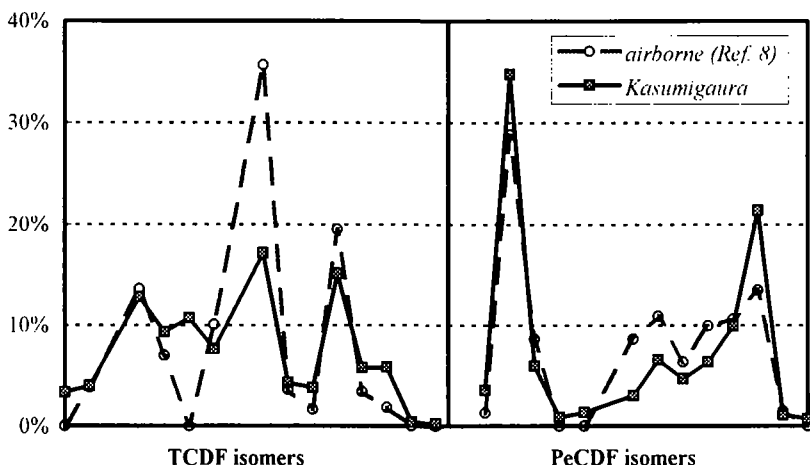
Figure 3: TCDF and PeCDF isomer patterns. The isomer (or isomers) are plotted in the order of GC elution and by the ratio to the corresponding homologue total value. *Kasumigaura* is the geometric mean of the 9 samples analyzed in this study. *Airborne* PCDD/F data are the sum of vapor-phase and particulate-bound concentrations reported in Ref. 8 (peak assignments were slightly modified according to Ref. 6). Isomers with lower loading values (<0.6) to PC-1, namely, 2468-TCDF, 13468/12468-PeCDF and 23468/12469/12347/12346-PeCDF, are excluded from the plot.

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(Shintone River) than for the paddy-field sample.

L2 (TK Bay) sediment has the highest PC-3 score. The difference between L2 and other lake sediments may be explained by the fact that the entrance to TK Bay is narrow and thus the bay is isolated from other parts of the lake to some extent. It is unexpected that the paddy-field-soil sample shows the lowest score, because a large portion of PCP had been used as paddy-field herbicide. Almost 20 years have passed since the cessation of the production of PCP, and constant farming and soil runoff might have contributed to lowering the amount of PCP-derived PCDD/Fs in paddy-field soil, or the sampled paddy field may not be representative of this area.

Table 2: Principal component scores

Sample type	Sampling points	PC scores		
		PC-1	PC-2	PC-3
Lake sediment	L1	1.42	-0.24	0.31
	L2	0.60	-0.08	1.71
	L3	1.35	-0.37	0.29
	L4	0.53	-0.33	-0.78
River sediment	R1	-1.34	-1.03	-0.05
	R2	-1.02	-0.28	-0.06
	R3	-1.01	-1.11	-0.31
	R4	-0.78	2.30	0.88
paddy field soil		0.24	1.14	-2.00

Conclusions

Principal component analysis was applied to the data matrix obtained from isomer-specific determination of PCDD/Fs in sediment and soil samples from a freshwater lake area. Three major PCs were extracted. PC-1 accounts for 39% of the total variance and is designated as input from airborne PCDD/Fs. PC-2, which represents the variance by PCDD/Fs from the herbicide CNP, accounts for 22% of the total variance. PC-3 accounts for 22% of the variance and is interpreted to represent PCDD/Fs from PCP. Although potential contributions of unseparated sources or environmental transformation cannot be excluded, PCDD/Fs in sediment and paddy-field soil in this area can be concluded to originate mainly from these three sources. These readily interpretable PCs indicate the robustness of the analysis presented here, in spite of the limited number of samples. The interpretations of PCs largely depended on the information from non-2378 compounds, demonstrating the validity of the analysis which includes these compounds. PC scores behave differently depending on the nature of the sample, suggesting the environmental fate of the compounds. These results suggest that a further application of multivariate analysis to isomer-specific PCDD/F data set can give a quantitative estimate of the contributions of the different kinds of sources to the PCDD/F concentration in the general environment.

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