MULTIVARIATE DATA ANALYSIS OF DIOXINS IN DATED SEDIMENT CORES COLLECTED IN THE KANTO REGION OF JAPAN

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Introduction

Past dioxin flux as recorded in aquatic sediment is important in understanding the current status of dioxin pollution. Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in sediment cores have been studied in many regions of the world[1], including Japan[2]. Recently, the Japan Environment Agency (JEA) investigated PCDDs and PCDFs as well as several non-ortho and mono-orhto substituted polychlorinated biphenyls (Co-PCBs, those with toxic equivalency factors by the WHO in 1998[3]) in dated cores[4]. In this paper, 2,3,7,8-substituted PCDDs and PCDFs, and Co-PCBs are collectively referred to as dioxins.

We analyzed the JEA data using principal component analysis (PCA). PCA transforms original variables into their linear combinations (principal components, PCs), which are orthogonal to each other and account for decreasing proportions of the data variance. Its general objectives are data reduction and interpretation. In this study, the general trend in flux of the 29 dioxin compounds will be summarized in a few PCs and will consequently be discussed in a more comprehensible form in terms of 1) the differences among the sampled areas and 2) the time trends of dioxin flux.

Materials and Methods

Data for 2-cm-thick 78 subcores were reported for seven 2,3,7,8-substituted PCDDs, ten 2,3,7,8-substituted PCDFs and twelve Co-PCBs[4]. Subcores were dated using the ^{210}Pb technique. A brief description of the 4 core samples from the Kanto region of Japan analyzed in this study are given in Table 1. Input flux ($pg/cm^2\cdot yr$) of each compound, which was calculated as the product of the concentration of the compound (pg/g) and the sedimentation flux ($g/cm^2\cdot yr$)[4], was used for the analysis because flux rather than concentration reflects dioxin inputs to the aquatic sediment.

The 29 compounds were treated as variables and the 78 subcores as cases. Normal or log-normal distributions cannot be expected for the variables because the data set consists of 4 cores from 3 different areas. However, log transformation improved overall symmetry of the variable distributions, and thus, log-transformed values were subjected to PCA. Log transformation enabled us to deal with large difference in flux of the compounds among both subcores and cores at the cost of sensitivity for small differences in the data values.

Values not detected (N.D.) were excluded from the PCA as follows. Four compounds (2,3,7,8-TeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,7,8,9-HxCDF and 3,3',4,4',5,5'-HxCB) with a high incidence (>25% of all subcores) of N.D. were removed. For the remaining 25 variables, cases with N.D. values were removed from the analysis (case-wise deletion). As a result, 58 out of 78 subcores were used for the analysis.

The variance of each variable was normalized to unity by using the correlation matrix as the input to PCA, to focus on the relative variation. The eigenvectors were normal-varimax rotated to improve the interpretability of the results[5]. Statistical analyses were carried out on Statistica for *Windows ('98 ed. release 5.1, StatSoft, 1998) and SPSS for Windows (8.0.1J, SPSS, 1998).*

Results and Discussion

Generally, older subcores were removed from the analysis because of a higher incidence of N.D. values; 8 subcores before 1963 from TB-stB, 5 subcores before 1946 and the 1962 subcore from Kasumi-stD and 6 subcores before 1950 from Haruna were removed. Therefore, the discussion below corresponds to the dioxin flux in the later half of the 20th century. It is worth noting that the Kasumi-stD core has a relatively deep surface mixing depth that corresponds to about 35 years. Time resolution of this core should be much lower than the other 3 cores, if this depth of surface mixing is also typical of previous periods.

After varimax rotation, PC-1, PC-2 and PC-3 accounted for 53%, 31% and 14% , respectively, and 98% in total, of the total standardized variance of log-transformed data. Each of the other PCs accounted for less than 1.5%. Thus, the number of PCs was determined to be 3.

Factor loading values for PCs-1 to 3 are summarized in Table 2. PC-1 is characterized by high ($r > 0.7$) correlation with all the Co-PCBs, as well as with 2,3,7,8-TeCDF and 1,2,3,7,8-PeCDF. PC-2 is highly correlated with most of the penta- to hepta-2,3,7,8-substututed CDFs as well as with 1,2,3,7,8-PeCDD. PC-3 is characterized by modest ($0.7>r>0.5$) correlation with 2,3,7,8-substituted PCDDs. All the factor loading values for PCs-1 to -3 are greater than zero.

Figure 1 shows projections of the subcores on 2-dimension PC planes of PCs 1 and 2 (Figure 1-a) and PCs 1 and 3 (Figure 1-b). The subcores form clusters according to the sampled area in both Figures 1-a and 1-b, suggesting that the cores from different sampling areas exhibit distinct dioxin compositions. The high PC-1 score for the subcores from Tokyo Bay corresponds to a higher dioxin flux, especially of Co-PCBs, in this area than in the other two areas. A large population and intense industrial and municipal activities in the catchment area of Tokyo Bay indicate high PCB formulation usage and incineration activity both of which are considered as Co-PCB sources, and thus higher Co-PCB flux. The PC-2 score is lower in older subcores and higher in newer ones of all 4 cores. Thus, PC-2 can be interpreted to reflect a common change in dioxin flux over time in the Kanto region. The Kasumigaura core can be distinguished from the Haruna core by higher 1,2,3,4,6,7,8-HpCDD and OCDD fluxes, which are reflected in their PC-3 scores.

The limitations of the analysis presented here may include lack of origin-specificity in the given data set which consists of only 2,3,7,8-substituted PCDDs and PCDFs and Co-PCBs. Inclusion of other (non-2,3,7,8-substituted or non-coplanar) compounds may be necessary to discuss the dioxins in the analyzed cores in terms of their origins[5].

Conclusion

PCA of dioxin flux recorded in 4 dated cores from 3 different areas in the Kanto region of Japan resulted in 3 major PCs which in total account for 98% of the data variance. The subcores form clusters by the sampled area in the PC score plots, suggesting that the cores from different sampling areas exhibit distinct dioxin compositions. The high PC-1 score for the subcores from Tokyo Bay corresponds to a higher dioxin flux, especially of Co-PCBs, in this area than in the other two areas. PC-2 can be interpreted to reflect common change in dioxin flux over time in the Kanto region. The Kasumigaura core can be distinguished from the Haruna core by higher HpCDD and OCDD fluxes, which are reflected in their PC-3 scores.

References

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Table 1. Brief description of the analyzed core.

sampled area	core code	number of subcores and the oldest year[a]	catchment area
Tokyo Bay	TB-stB	20 (1905/1963)	densely inhabited (34 capita/ha) with a wide variety of municipal, agricultural and industrial activities.
	TB-stD	20 (1959/1959)	
Lake Kasumigaura	Kasumi-stD	20 (1925/1946)	mainly agricultural area.
Lake Haruna	Haruna	18 (1832/1950)	mountain top, can be considered as background.

[a](oldest dated year/oldest year analyzed in this paper)

Table 2. Factor loading values for PCs 1 to 3. (++: r>0.7, +: 0.7>r>0.5, •: 0.5>r>0)

compounds	PC-1	PC-2	PC-3	compounds	PC-1	PC-2	PC-3
1,2,3,7,8-PeCDD	•	++	+	OCDF	++	•	•
1,2,3,6,7,8-HxCDD	+	+	+	3,3',4,4'-TeCB	++	•	•
1,2,3,7,8,9-HxCDD	•	+	+	3,4,4',5-TeCB	++	•	•
1,2,3,6,7,8-HpCDD	+	•	+	3,3',4,4',5-PeCB	++	•	•
OCDD	+	•	+	2,3,3',4,4'-PeCB	++	•	•
2,3,7,8-TeCDF	++	•	•	2,3,4,4',5-PeCB	++	•	•
1,2,3,7,8-PeCDF	++	+	•	2,3',4,4',5-PeCB	++	•	•
2,3,4,7,8-PeCDF	+	++	•	2',3,4,4',5-PeCB	++	•	•
1,2,3,4,7,8-HxCDF	+	+	•	2,3,3',4,4',5-HxCB	++	•	•
1,2,3,6,7,8-HxCDF	•	++	•	2,3,3',4,4',5'-HxCB	++	•	•
2,3,4,6,7,8-HxCDF	•	++	•	2,3',4,4',5,5'-HxCB	++	•	•
1,2,3,4,6,7,8-HpCDF	+	+	•	2,3,3',4,4',5,5'-HpCB	++	+	•
1,2,3,4,7,8,9-HpCDF	+	++	•	contribution	53%	31%	14%

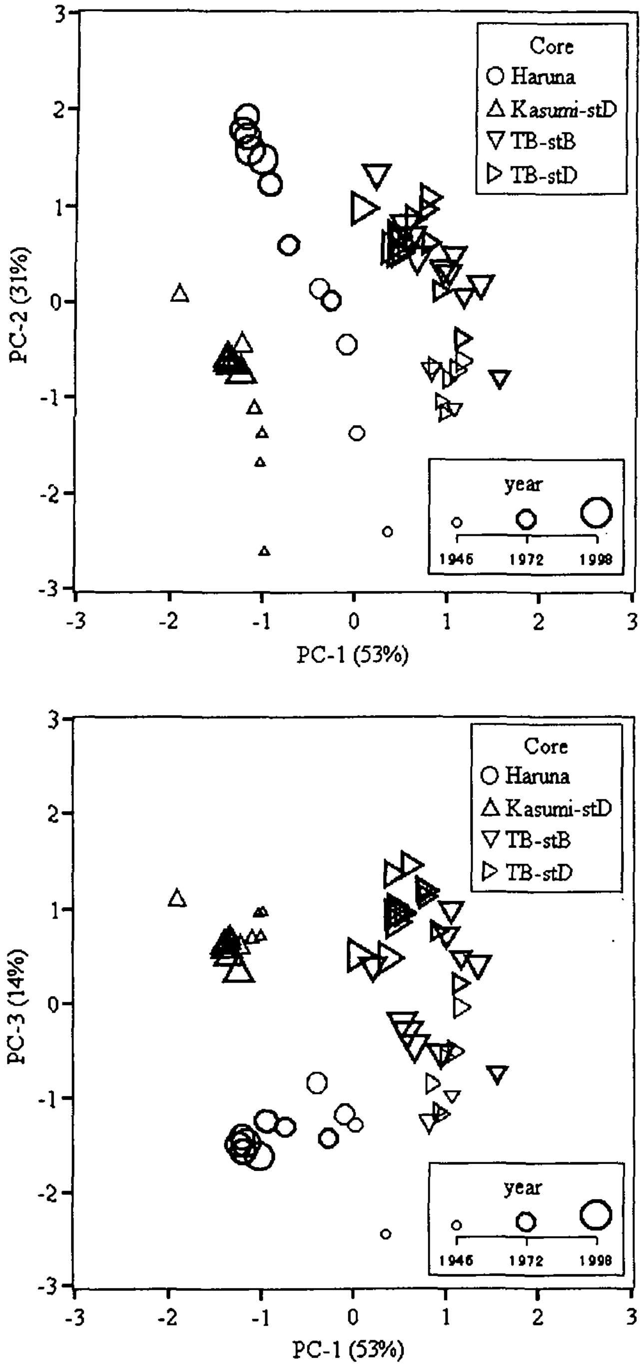

Figure 1. PC score plots for PCs-1 and -2 (Figure 1-a: top) and for PCs-1 and -3 (Figure 1-b: bottom).