

Origin Estimation of Dioxins in Japanese Environment Using Multivariate Statistical Methods

Takeo Sakurai¹, Noriyuki Suzuki², Shigeki Masunaga³ and Junko Nakanishi³

¹ National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba, Ibaraki 305, Japan

² Kanazawa Institute of Technology, 7-1 Ohgigaoka, Nonoichi, Ishikawa 921, Japan

³ Yokohama National University, 79-7 Tokiwadai, Hodogaya, Yokohama, Kanagawa 240, Japan

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Abstract

The PCDDs and PCDFs in sediment and soil from the Kanto region were isomer-specifically determined and the obtained data were analyzed using principal component analysis (PCA) to estimate the major origins of these compounds. Four major PCs were obtained and attributed to PCDDs and PCDFs in aerial deposition, herbicide CNP and pentachlorophenol, while one PC remained unattributed. The PC scores indicated relative influence of these origins.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are distributed worldwide (Webster and Commoner, 1994). Among them are extremely toxic compounds, and people all over the world are exposed to these compounds at relatively low levels (Takayama *et al.*, 1991; Startin, 1994). However, results of some animal experiments suggest a toxic effect at doses relevant to our daily exposure level (Rier *et al.*, 1993). A comprehensive understanding of the environmental fate of these compounds from their sources to exposure pathways will help to effectively control our exposure to these compounds.

The major part of PCDDs and PCDFs are believed to be distributed to and accumulate in sediment or soil in the general environment as a result of their lipophilic nature and their persistence in those matrices (Mackay *et al.*, 1992). Thus, sediment and soil can be considered

as conservative matrices which record the PCDD and PCDF input to the environment. A detailed examination of PCDDs and PCDFs in these matrices may contribute to the understanding of the environmental fate of these compounds. In this paper, the word 'origin' is used to refer to the various inputs of PCDDs and PCDFs to environmental matrices and not to the emission sources of these compounds.

Since PCDDs and PCDFs are made up of 210 congeners, analysis of these compounds yields a considerable amount of data. Multivariate statistical analyses have been utilized to reduce the complexity of the data. Principal component analysis (PCA) has been applied successfully to group the samples or to reveal the proximity between the source and environmental samples. However, only a few researchers have tried to relate the obtained principal components (PCs) to the sources/origins of these compounds (Yamamoto, 1994; Ehrlich *et al.*, 1994). In most of those applications, only the homolog total values and/or concentrations of 2,3,7,8-substituted compounds were used. The inclusion of other isomers as input variables may result in a more comprehensive analysis of the data matrix structure (Evers *et al.*, 1989; Creaser *et al.*, 1990).

Recently, Brzuzy and Hites (1996) reported a gap between the emission flux to the atmosphere and the aerial deposition flux of PCDDs and PCDFs on a global scale (i.e., deposition is 4 times greater than emission). They also presented a considerable disparity in the homolog compositions for the representative sources and for soil or sediment. In Japan, limited source inventories have become available only recently, and more quantitative information is required, especially regarding the source/origin and environmental fate of PCDDs and PCDFs.

In this study, the PCDDs and PCDFs in sediment and soil from two areas in the Kanto region were isomer-specifically determined and the obtained data were analyzed using a multivariate statistical method to estimate the major origins of these compounds in these areas.

2. Materials and Methods

2.1 Determination of PCDDs and PCDFs

Fifteen sediment samples and two soil samples were collected in and around two major water systems in the Kanto region, namely, Lake Kasumigaura and Tokyo Bay (Fig. 1). The Kanto region is densely inhabited (approx. 10 capita/ha) so that the samples are expected to be impacted by many kind of human activities. The sediment sampling points were selected to represent the spatial distribution of PCDDs and PCDFs in the Lake Kasumigaura area and the Tokyo Bay area. A paddy-field soil and an urban soil sample were also included in the analysis to represent the impact of agricultural and urban activities, respectively.

Sampling and determination of PCDDs and PCDFs followed the procedure described previously (Sakurai *et al.*, 1996). Purified extracts were isomer-specifically analyzed for tetra-

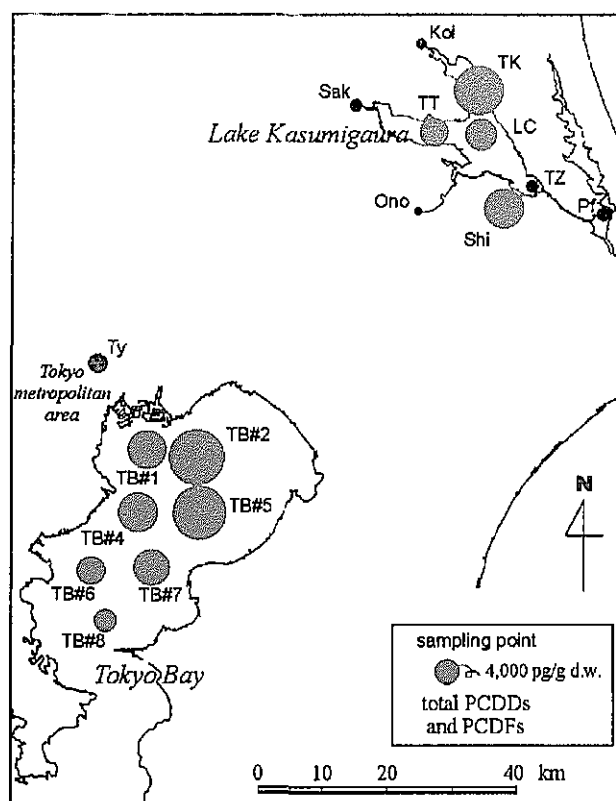


Fig. 1. Sampling points and total PCDD and PCDF concentrations

to octa-chlorinated PCDDs and PCDFs by high-resolution gas chromatography/high-resolution mass spectrometry using a DB-5 (60 m × 0.25 mm i.d., J&W Scientific) column.

2.2 Principal component analysis (PCA)

From 87 chromatographic peaks on DB-5, which represent isomers or isomer clusters, 73 peaks of reliable quantitation (i.e., without samples below detection limits or samples with interference) were subjected to PCA. The peak concentrations were normalized to ignition losses (at 600 °C × 1 hr after drying) to reduce the effect of the difference in concentrations among the samples. The variance of each peak was normalized to unity 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. Statistical analyses were carried out on Statistica for Windows 5.0J (StatSoft. Inc., 1996) and SPSS for Windows 6.0 (SPSS Inc., 1993).

3. Results and Discussion

3.1 PCDD and PCDF concentrations

The total PCDD and PCDF concentrations in sediment and soil samples ranged from 377

to 20,300 pg/g dry matter (Fig. 1). When normalized to ignition loss, the total concentration range was from 12,700 to 188,000 pg/g ignition loss, reduced from a 54-fold difference to a 15-fold difference.

3.2 Description of the principal components (PCs)

After varimax rotation, PC-1, PC-2, PC-3 and PC-4 accounted for 53%, 16%, 17% and 9.0% of the total standardized variance, respectively. Each of the other PCs accounted for less than 1.5%. Thus, the number of PCs was determined to be four. Descriptions of the four major PCs, which account for 95% of the total variance altogether, are summarized in Table 1. For PCs-1 to -4, most of the factor loading values were greater than zero, and all loading values were greater than -0.3, with only one being smaller than -0.2.

3.3 Source attribution for the PCs

Calculated PCs were interpreted by isomeric comparison to authentic references. The group of compounds with a high correlation to a PC can be considered to behave together in the studied areas. The four PCs account for the major part of the variance of organic-matter-normalized data and may thus represent the major origins of PCDDs and PCDFs in the Kanto region. The composition of the compounds with high factor loading values ($r > 0.7$) to a PC was compared to that in the literature to attribute the PC to a specific origin.

Although PCDDs and PCDFs are considered stable in sediment and soil, they may undergo selective enrichment or loss of some congeners during transportation. These potential changes were not taken into account in the following discussion.

1) PC-1

Fig. 2 shows TCDF, PeCDF and HxCDF isomer patterns of the typical samples analyzed in this study and of the aerial deposition collected in the same area (Ogura, 1998). Isomers or isomer clusters with low loading values ($r < 0.5$) with PC-1 are removed from the plot to exclude the impact from other origins. The similarity between the sediment isomeric patterns and those in aerial deposition suggests that PC-1 represents the aerial input of PCDDs and PCDFs.

Aerial depositions in another part of Japan were reported to contain tetra- to hexa-CDFs as major components of PCDFs (Kurokawa *et al.*, 1992). Aerial deposition has been considered as one of the major PCDD and PCDF inputs to sediment (Czuczwa and Hites, 1986). These two findings support the link between PC-1 and the PCDDs and PCDFs in atmospheric deposition.

It must be noted that this attribution does not necessarily imply direct deposition of these compounds to the sampling sites. Once deposited PCDDs and PCDFs may have been conveyed by sediment transport, resuspension or other transport processes.

Table 1. Descriptions of calculated principal components (PCs)

PC	1	2	3	4
contribution	53%	16%	17%	9.0%
characteristic compounds ¹⁾	most of the 4- to 6-CDFs	4- and 5-CDDs/CDFs related to 1368- or 1379- Cl substitution	5- to 7-CDD isomers with 1269- Cl substitution	several 6- to 8-CDD/CDF isomers
origin attribution	aerial deposition ²⁾	CNP ³⁾	undetermined	PCP ⁴⁾

1) isomers or isomer clusters with high loading values ($r > 0.7$); however, no isomers or isomer clusters showed correlation greater than 0.7 for PC-4, and those with loading values greater than 0.6 are described. 2) Ogura (1998). 3) Yamagishi *et al.* (1981). 4) Hagenmaier and Brunner (1987)

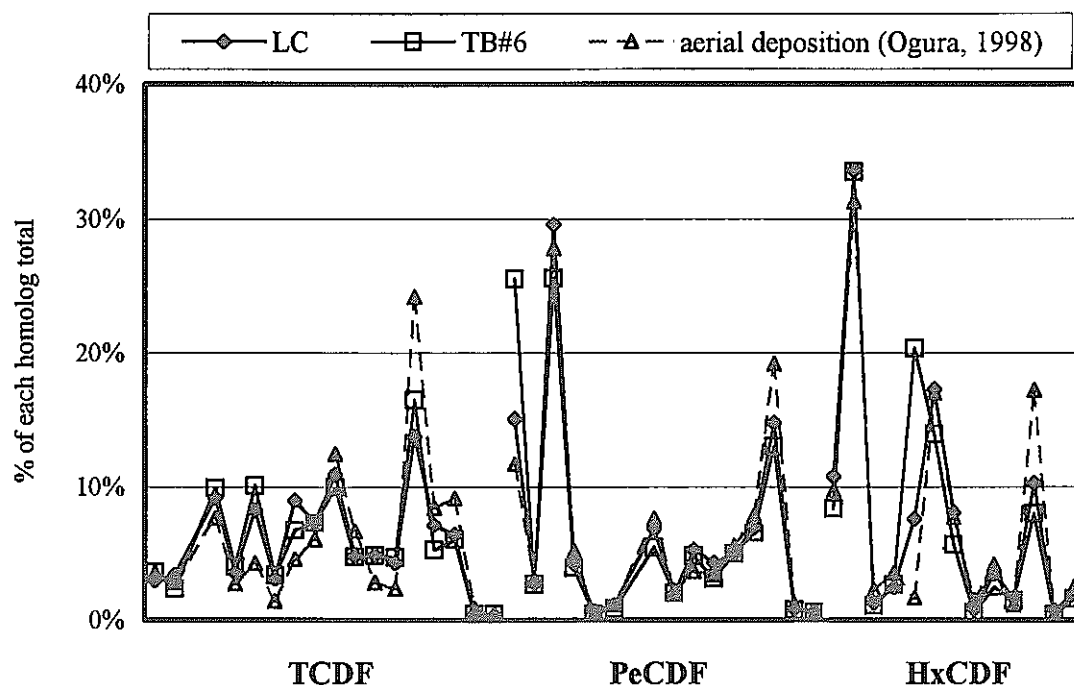


Fig. 2. TCDF, PeCDF and HxCDF isomer patterns for typical sediment and aerial deposition: The isomers (or isomer clusters) are plotted in the order of gas-chromatographic elution and as the ratio to the corresponding homolog total. LC and TB#6 sediment samples were analyzed in this study. Depositional PCDDs and PCDFs in Tokyo were determined by Ogura (1998). Isomers or isomer clusters with low loading values ($r < 0.5$) to PC-1, namely, 2,4,6,8-TCDF and 2,3,4,6,8/1,2,4,6,9/1,2,3,4,7/1,2,3,4,6-PeCDF, are excluded from the plot.

2) PC-2

Yamagishi *et al.* (1981) reported 1,3,6,8-TCDD; 1,3,7,9-TCDD and 2,4,6,8-TCDF, resulting from chemical by-reactions of chlorophenols, as the main components of PCDDs and PCDFs in the herbicide CNP (1,3,5-trichloro-2-(4-nitrophenoxy) benzene). Each eleven isomer or isomer cluster with a high correlation to PC-2 contains a compound(s) that is structurally related to 1,3,6,8- or 1,3,7,9- (or equivalent) chlorine substitution. Therefore, PC-2 is interpreted to represent the PCDDs and PCDFs that originate from the herbicide CNP.

More than 70,000 tons of CNP had been applied in Japan, mainly to paddy fields, until a practical ban of its use in 1994. CNP was reported to contain about 1,700 and 140 $\mu\text{g/g}$ of TCDDs and TCDFs, respectively (Yamagishi *et al.*, 1981). Paddy fields comprise about 10% of the Kanto region. Hence, it is reasonable that the CNP-derived PC accounts for a considerable part of the total variance.

3) PC-3

All seven isomers or isomer clusters of penta- to hepta-CDDs with a high correlation to PC-3 are characterized by 1,2,6,9- (or equivalent) chlorine substitution. However, the authors were not able to attribute this composition to any reported origin or transformation process of PCDDs and PCDFs. Although PC-3 is referred to as origin in this paper, this may represent either some input or lack of some loss/transformation.

4) PC-4

PC-4 is interpreted to represent the pentachlorophenol (PCP)-derived PCDDs and PCDFs, because six compounds with the highest correlation ($r > 0.6$) to this PC, namely 1,2,4,6,8,9-HxCDF; 1,2,3,4,6,7,8-HpCDF; 1,2,3,4,6,8,9-HpCDF; 1,2,3,4,6,7,8-HpCDD; OCDF and OCDD, were reported to be the main constituents of PCDDs and PCDFs in PCP (Hagenmaier and Brunner, 1987). About 175,000 tons of PCP had been sold in Japan until its production decreased dramatically in early 1970's. It is not surprising that PCDDs and PCDFs originating from PCP still remain in the environment, considering the persistence of these compounds.

3.4 Origin contribution

PC scores, a normalized measure of variation from the mean value for each PC, are shown in Table 2 for each sample. The PC scores indicate the relative intensity of the influence of the corresponding origin among samples. In this analysis, high scores for PC-1, PC-2 and PC-4 indicate more input than loss from atmospheric, CNP-derived and PCP-derived PCDDs and PCDFs on an organic-matter basis, respectively.

Several interesting geographical distributions were found to exist. In Tokyo Bay, samples from the western part (TB#1, #4, #6) showed higher scores for PC-1 and lower scores for PC-4,

than their eastern counterpart (TB#2, #5, #7). In the Lake Kasumigaura area, the PC-4 scores suggest a generally higher contribution from PCP for river sediments than for lake sediments. In contrast, the PC-3 scores in the Kasumigaura area were high for lake sediments, especially for TK and LC. These geographical trends require more detailed examination in connection with related factors such as environmental transport process and emission inventory and history.

4. Conclusion

PCA was applied to the data matrix obtained from isomer-specific determination of PCDDs and PCDFs in sediment and soil samples to estimate the origins of these compounds in the Lake Kasumigaura and Tokyo Bay areas.

Four major PCs, which accounted for 95% of the total variance altogether, were extracted and attributed to specific origins by isomeric comparison with references. PCs-1, 2 and 4 were interpreted to represent PCDDs and PCDFs from atmospheric deposition, herbicide CNP and PCP. It was not possible to attribute PC-3 to any reported origin or transformation process of PCDDs and PCDFs. Together with additional information about the attributed origins and the target areas, it can be concluded from our PCA that PCDDs and PCDFs in sediment and soil in these areas mainly emanate from these four origins. The relative contributions of these four origins were indicated by the PC scores.

These readily interpretable PCs indicate the robustness of the analysis presented here, despite the limited number of samples. The interpretations of PCs largely depended on the information from non-2,3,7,8-substituted compounds, demonstrating the validity of the analysis which included these compounds. The method applied in this study was effective in elucidating

Table 2. Principal component scores

		PC-1	PC-2	PC-3	PC-4
Kasumigaura Lake	LC	▽	▽	○	▽
	TK	▽	•	⊙	▽
	TT	▽	▽	•	▽
	TZ	▽	•	▽	•
Kasumigaura River	Koi	▽	•	▽	○
	Sak	▽	•	▽	•
	Ono	▽	▽	▽	○
	Shi	•	⊙	•	▽
soil	Pf	▽	○	•	▽
	Ty	○	▽	▼	▽
	TB#1	⊙	•	•	▽
Tokyo Bay	TB#2	○	○	○	⊙
	TB#4	○	•	•	○
	TB#5	○	•	•	⊙
	TB#6	○	•	•	▽
	TB#7	•	•	•	○
	TB#8	•	•	•	•

▽ < -1.5

-1.5 ≤ ▽ < -0.5

-0.5 ≤ • < 0.5

0.5 ≤ ○ < 1.5

1.5 ≤ ⊙

the origins of PCDDs and PCDFs based on the composition of these compounds in environmental matrices.

5. Acknowledgment

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