SOURCE IDENTIFICATION OF DIOXINS IN RAW WATER FOR DRINKING

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Introduction

Well-known sources of dioxins and furans to receiving waters include point sources such as discharges from industrial incinerators and industrial facilities, e.g. effluents from pulp and paper mills and wood treating facilities, sewer plants as well as diffuse inputs like run-offs from street, agrochemicals from paddy field. As PCDDs and PCDFs are poorly soluble in water and have high Koc values they do not stay in the aqueous phase but strongly adsorb to particles. Sediments of rivers, lakes and oceans are the ultimate sinks for water-borne dioxins and furans. Since PCDDs/DFs are made up of 210 congeners, analysis of these compounds yields a considerable amount of data. Multivariate analysis has been utilized by many researchers to reduce the complexity of the data. Okumura et al. (2004) and Masunaga et al (2001) reported the PCDDs/DFs profile from sediment samples and agrochemicals. Minomo et al. (2011) and Kjeller et al. (1996) have used Principal Component Analysis (PCA) to study the fingerprints of dioxins in environmental samples, and deduced the typical patterns for combustion sources etc. Rigo et al. (1995) have used a combination of chemometric methods including multiple regression analysis, PCA and hierarchical cluster analysis to examine the relationship between chlorine levels in waste stream and dioxins emissions from combustor stacks. Therefore, this study investigated the source identification of dioxins and compared the dioxins data, which is 149 raw water samples collected from 45 water treatment plants, using hierarchical cluster analysis and PCA.

Materials and methods

Sample Collection

Raw water samples totaling 149 were collected from 45 water treatment plants throughout Japan over three years. The water source for 40 of the water treatment plants is surface water and the remaining 5 water treatment plants are fed by ground water.

Data Analysis

Cluster analysis and PCA were computed by the software, Statistica. Normalization of samples was not applied. From the 84 chromatographic peaks on BPX-5 and BPX-50, which represent isomers or isomer clusters, 83 peaks of reliable quantitation were subjected to cluster analysis and PCA. When a result was under the quantitation limit, the congener was assumed to be present at one-half of the detection limit. Samples consisted of 40 surface water samples and 5 ground water samples. The mean concentration, which was divided by the frequency of sampling, was applied to hierarchical cluster analysis and PCA.

Results and discussion

Score Plot of Dioxins by PCA

Fig. 1 shows the score plot of PCDDs/DFs and Co-PCBs from factor analysis with the PCA. The first principal component (PC 1) explains 66% of the total variance, while the second principal component (PC 2) accounts for 12%. PC 1 and PC 2 together account for 78% of the total variance, therefore it is considered that Fig. 1 contains most of the original information about the dioxins homologue distribution. It can be seen that the data points for each sector are clustered together. The PC 1 represents the PCDDs and PCDFs and the PC 2 represents the Co-PCBs. Therefore, these homologue profiles are similar although there are some differences between the sectors. Fig. 2 also shows that surface and ground water can be divided into different clusters. PC 1 shows the features of surface water and the score of ground water is very low. This result shows that the cluster can be divided with 2 groups such as surface water and ground water.

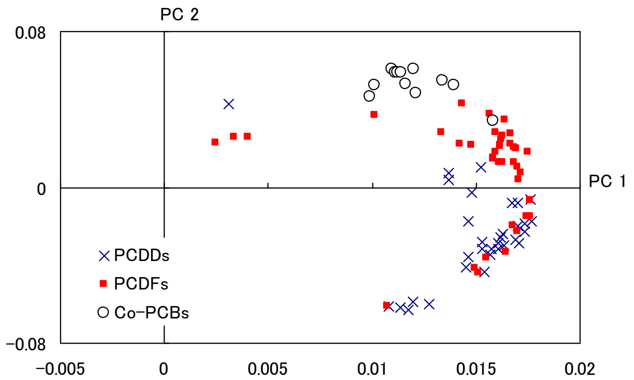

Fig. 1 Score plot of Dioxins by the PCA

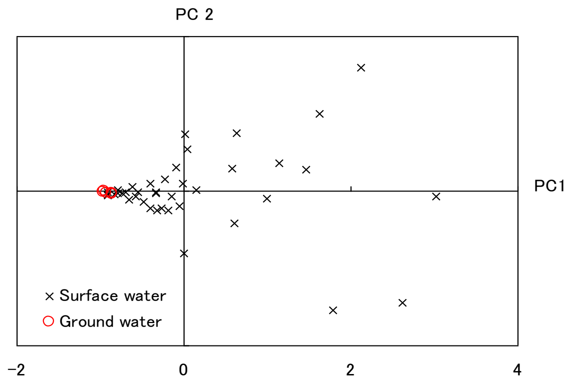

Fig. 2 Score plot of Surface and Ground water from the PCA

Regional Distribution by Hierarchical Cluster Analysis

Fig. 3 shows the result of hierarchical cluster analysis with the cluster method of Ward' method. There are three big clusters form group 1 to group 3. In the view of the total dioxins concentration, the group can be divided clearly. Every group shows totally different dioxins concentration. The average concentrations of every group were 139pg/L (70 ~ 261pg/L), 46pg/L (30 ~ 68pg/L) and 13pg/L (2 ~ 27pg/L), respectively. Each group has individual features: group 1 shows agricultural areas in Japan (particularly, CN1, KI3 and KK3), group 2 represents industrial areas (KT5, KT6 CH2 and TN3), and group 3 indicates background areas like uncontaminated areas.

PCA Results of Each Group

It was identified by hierarchical cluster analysis that each group has some features such as agricultural, industrial and uncontaminated areas. Therefore, we need to confirm the similarities in dioxin profiles in each group. Calculated PCs were interpreted through conger-specific comparison to authentic references and the results of PCP and CNP examined. The composition of the congeners with a high factor loading value (r> 0.7) to a PC was compared to that in literature to attribute the PC to a specific origin.

In Group 1, generally representing the agricultural area and after varimax rotation, PC 1, PC 2, PC 3 and PC 4 accounted for 34%, 24%, 18% and 6% of the total standardized variance, respectively. Descriptions of the four major PCs, which account for 82% of the total variance, are shown in Table 1. PC 1, with a contribution rate of 34%, showed characteristic congeners like TeCDFs, PeCDDs, PeCDFs and HxCDFs, which represent combustion sources. Sakurai et al. (1998), Eitzer and Hites (1989) reported that TCDF, PeCDF and HxCDF isomer patterns of the samples are from the airborne PCDDs/DFs. PC 2, with a contribution rate of 24%, indicated characteristic congeners like 1,3,6,8-, 1,3,7,9-, 13,6,9-TeCDDs, 2,4,6,8-TeCDF and particularly 1368,1379-substituted PeCDDs and TeCDFs, which represent CNP. The result of this study as well as some previous reports showed 1,3,6,8-, 1,3,7,9-, 1,3,6,9-TeCDD and 2,4,6,8-TeCDF, resulting from chemical by-reaction of chlorphenols, as the main components of PCDDs/DFs in the herbicide CNP (Masunaga et al., 2001, Yamagishi et al., 1981). PC 3, of which the contribution rate is 18%, indicated characteristic congeners like OCDD, OCDF, 1,2,3,4,6,7,8-HpCDF and 1,2,3,4,7,8-, 1,2,3,7,8,9-HxCDF, which represent PCP. Hagenmaier and Brunner (1987) reported these isomers are the main dioxins impurities of PCP. From the results, it is identified that Group 1 is an agricultural area with the contribution of 42% (CNP and PCP).

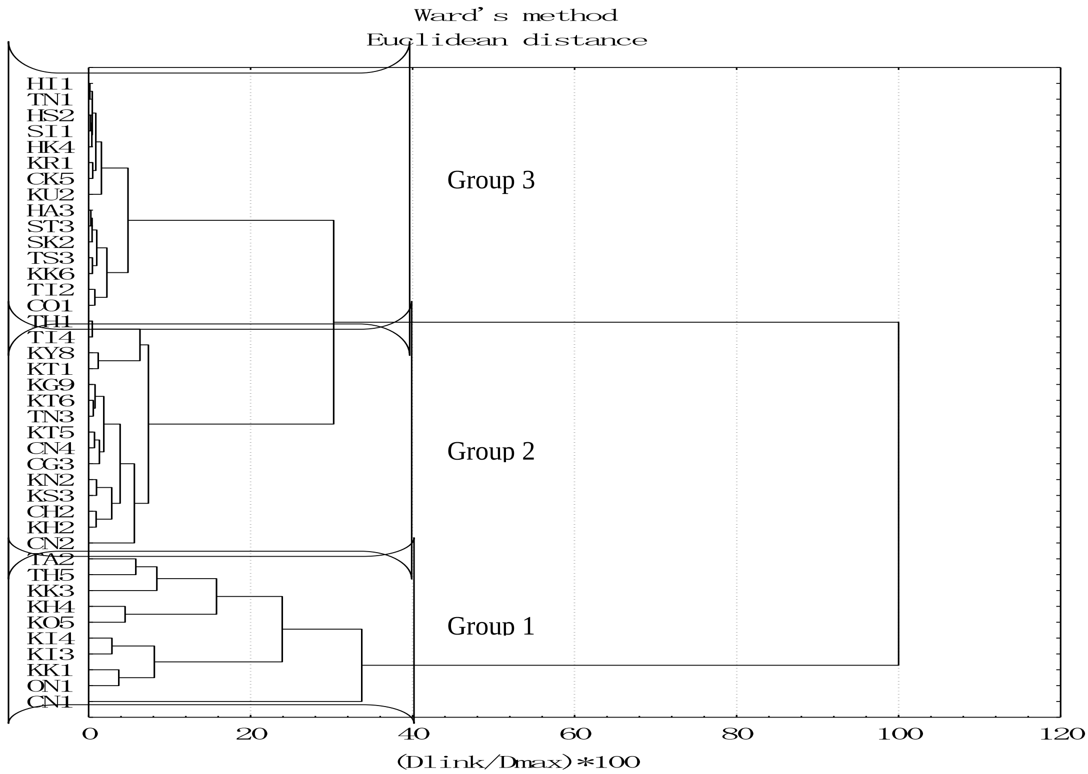

Fig. 3 Regional Distribution by hierarchical cluster analysis

Table 1. PCA results of group 1

PC	Contribution	Cumulative contribution	Characteristic congeners (Factor loadings > 0.7)	Interpretation
PC1	0.34	0.34	some of TeCDFs and PeCDDs, most of PeCDFs and HxCDFs	Combustion
PC2	0.24	0.58	some of TeCDDs, PeCDDs and 2468-TeCDF, especially 1368,1379-sustituted TeCDDs and TeCDFs	CNP
PC3	0.18	0.76	some of HxCDDs and HxCDFs, OCDD, OCDF	PCP
PC4	0.06	0.82	some of TeCDDs, and TeCDFs	Difficult

For Group 2, generally representing the industrial area, PC 1, PC 2, PC 3 and PC 4 accounted for 34%, 24%, 18% and 6% of the total standardized variance, respectively. Descriptions of the five major PCs, which account for 85% of the total variance, are shown in Table 2. PC 1, with a contribution rate of 41%, showed characteristic congeners like TeCDFs, PeCDDs, PeCDFs and HxCDFs, which represent combustion sources. PC 2 (12%)

indicated 1,3,6,8-, 1,3,7,9-, 13,6,9-TeCDDs and 1,2,36,8-, 1,2,3,7,9-PeCDD contained in CNP. PC 3, of which contribution rate is 11%, indicated characteristic congeners like some TeCDFs, which may represent combustion. PC 4 and PC 5 were difficult to interprit the sources.

Table 2. PCA results of group 2

PC	Contribution	Cumulative contribution	Characteristic congeners (Factor loadings > 0.7)	Interpretation
PC1	0.41	0.41	half of TeCDFs, most of PeCDFs and HxCDFs, some of HpCDFs	Combustion
PC2	0.12	0.53	1368, 1379, 1369-TeCDD, 12368, 12379-PeCDD	CNP
PC3	0.11	0.64	some of TeCDFs	Combustion
PC4	0.11	0.75	1268,1279-TeCDD, 12347, 12346-PeCDD	Difficult
PC5	0.10	0.85	some of HxCDDs, 1234678HpCDFs	Difficult

As regard to the Group 3, generally representing the background (uncontaminated) area, PC 1, PC 2, PC 3 and PC 4 accounted for 38%, 22%, 16% and 9% of the total standardized variance, respectively. Descriptions of the four major PCs, which account for 75% of the total variance. 4 sampling sites (HI1, HS2, HA3 and HK4) from Hokkaido and 3 (SI1, ST3 and SK2) from Shikoku area are the typical clean areas in Japan.

Conclusions

By the hierarchical cluster analysis, the group was clearly divided into three. Every group shows totally different dioxins concentration. The average concentrations of the groups were 139pg/L, 46pg/L and 13pg/, respectively. The groups are able to be defined as follows: group 1 shows agricultural areas, group 2 represents industrial areas and group 3 indicates clean areas. In Group 1, the contribution of PC 2 and PC 3 representing CNP and PCP was 42 %. PC 1 accounted for 34% of combustion source. In Group 2, the contribution of PC 1 representing combustion source was 41%. PC 2 (12%) indicated 1,3,6,8-, 1,3,7,9-, 13,6,9-TeCDDs and 1,2,36,8-, 1,2,3,7,9-PeCDD contained in CNP. Group 3 showed that PC 1, PC 2, PC 3 and PC 4 accounted for 38%, 22%, 16% and 9%, respectively.

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