Multivariate statistical analysis of PCDDs and PCDFs in Japanese aquatic sediments

Takeshi Yamamoto
Japan Quality Assurance Organization, Kansai Office
3-8-19 Mizuhai, Higashi-Osaka 578 Japan

Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are unintentional byproducts of chemical manufacturing processes and are also products of various combustion processes. Combustion is a major source of PCDDs and PCDFs in the environments. The use and discard of these chemicals also contaminates the environment.

The Environment Agency (EA) of Japan has been conducting a survey of pollution caused by harmful chemicals including PCDDs and PCDFs since fiscal year 1985. Survey results have been evaluated by the Expert Committee for the severity of hazards to health. The committee recommended that toxicological information be collected and that the sources and environmental fate of these chemicals be studied. Identification of the sources and evaluation of their contributions are important in policy making to reduce environmental pollution and thus to prevent adverse effects on health.

Many authors have used statistical procedures to characterize PCDD and PCDF sources. The congener pattern is used for that purpose and a combination of homolog and isomer patterns has been used with some success to elucidate the source profiles. The concentrations, homolog profiles and congener profiles of PCDDs and PCDFs in sediments taken from sampling points throughout Japan were compared with predicted source samples that included pesticides and soils taken from urban areas.

Methods

The survey data were obtained from the EA's annual reports[1)] and were compiled into a computer database. Sediment samples were taken from sampling areas remote from any potential point source. The sampling areas included 31 points: 10 rivers, 5 lakes, and 16 estuaries. Analysis of the urban soil samples was described previously[2)].

Principal components analysis was used to characterize similarities and differences in sediment samples. To minimize any statistical bias associated with the orders-of-magnitude differences in PCDDs and PCDFs concentrations, the data were normalized by expressing the concentration of individual congeners as a percentage of the combined sum of the concentrations of the PCDDs. Principal components analysis was done with the statistical software program STATISCA (StatSoft) run on a personal computer (Apple Macintosh Centris 650).

Loadings were used to describe the contribution of each homolog variable to the eigen vector. The scores from the first, second, and third principal components were used to plot the results in two or three dimensions.

Results and Discussion

PCDD and PCDF levels

The concentrations of the PCDDs and PCDFs in sediment sample are shown as TEQ (I-TEF) values in Figs. 1 and 2. Figure 1 shows the TEQ level of PCDDs and PCDFs in river and lake sediments and shows that sediments from lakes were more polluted with PCDDs and PCDFs than those from river stations (from 12 to 41 pg TEQ/g of dry matter vs. 0 to 22 pg TEQ/g dry sediment, respectively). Figure 2 shows the levels of PCDDs and PCDFs in estuary sediments. The concentrations in Tokyo and Osaka bay samples were higher than those in the samples from of other areas. This probably represents the contribution of the industrialized urban areas behind the bays.

Levels found in sediment samples from Japan are within the ranges already reported for other industrialized countries.

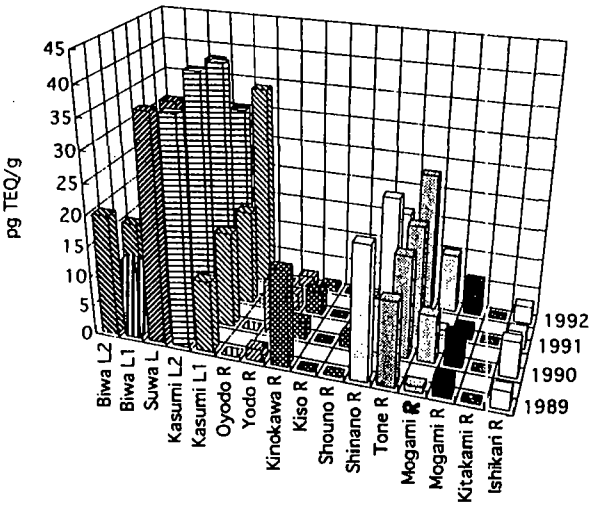

Fig. 1 Concentrations of PCDDs and PCDFs in lake (L) and river (R) sediments from FY 1989 to FY 1992.

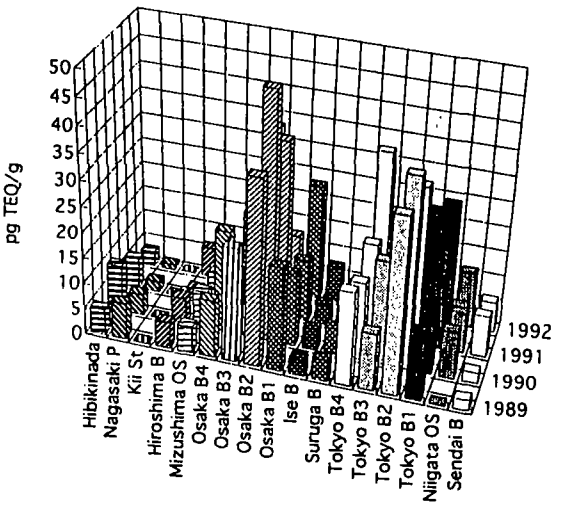

Fig. 2 Concentrations of PCDDs and PCDFs in estuary sediments from FY 1989 to FY 1992.

Congener profiles

Figure 3 shows homolog profiles from lake, river, and estuary sediments with some predicted source profiles (urban soil, pentachlorophenol: PCP and chloronitrophen: CNP). The congener profile from Kasumigaura lake sediment was very similar with that of PCP, and river sediment had a mixed pattern, between PCP and CNP. The homolog profiles of Tokyo Bay and of urban soil are similar, with the predominance of the higher chlorinated dioxin isomers giving "combustion" profiles. There seemed to be good correlations between sediment samples and predicted sources. However, except for these cases, many of the profiles are obscure with regarding to source characterization. This is because the sampling areas selected were remote from potential point sources and thus different sources contributed to each sample, and the ratios of these contributions varied as the distance from the sources increased.

Principal component analysis was used to distinguish the elements composing these data. Component loadings showed that there were three major principal components. Factor 1 accounted for 34% of the total variance, and indicated the atmospheric background group, mainly combustion sources. A second pattern is observed in the loadings for factor 2, which accounted for 23% of the total variance, and was characterized by hepta- and octa-CDDs that are involved in PCP. The third was characterized by tetraCDD isomers especially 1,3,6,8- and 1,3,7,9 -TCDD, which were major isomers found in some chlorinated diphenyl ether herbicides, e. g. CNP.

Factor scores for each sample were calculated and plotted in two or three dimensions. In Figure 4, one of these plots is presented. This figure shows three groups with different source characteristics. Group 1 had urban sources, and mainly included products of combustion processes, which have lower f2 and f3 scores, that is, Tokyo and Osaka

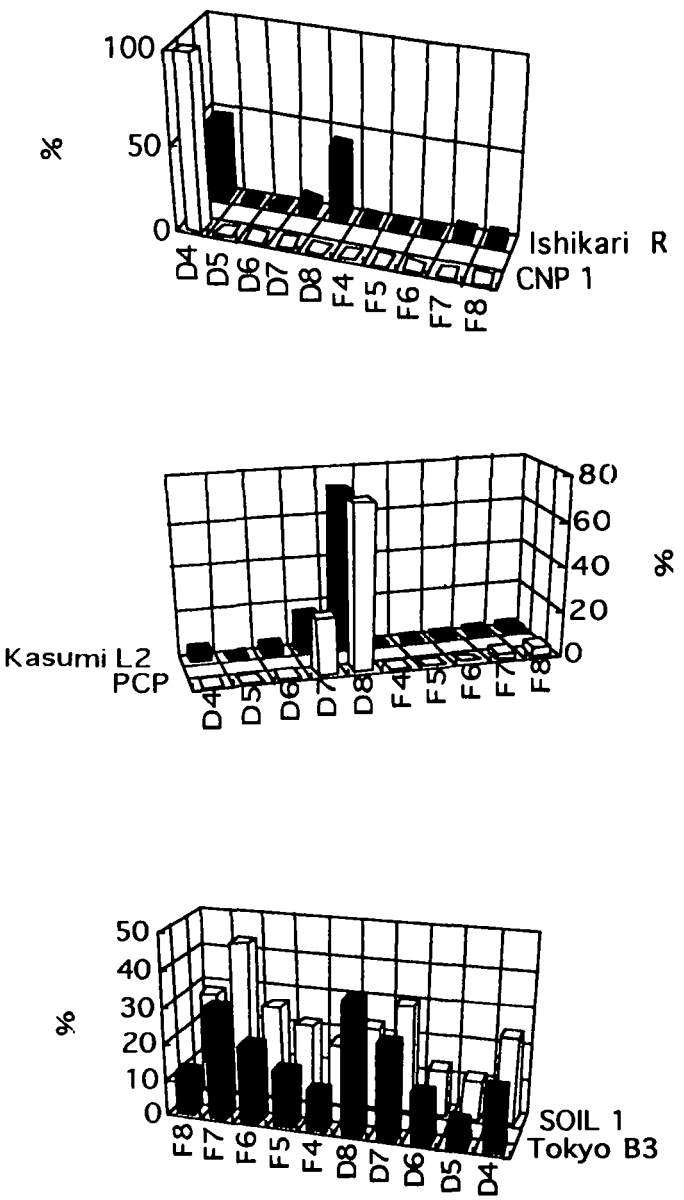

Fig. 3 Homolog profiles of sediments taken from a river (R), a lake (L) and on estuary (B), and of soil and pesticides (PCP, CNP).

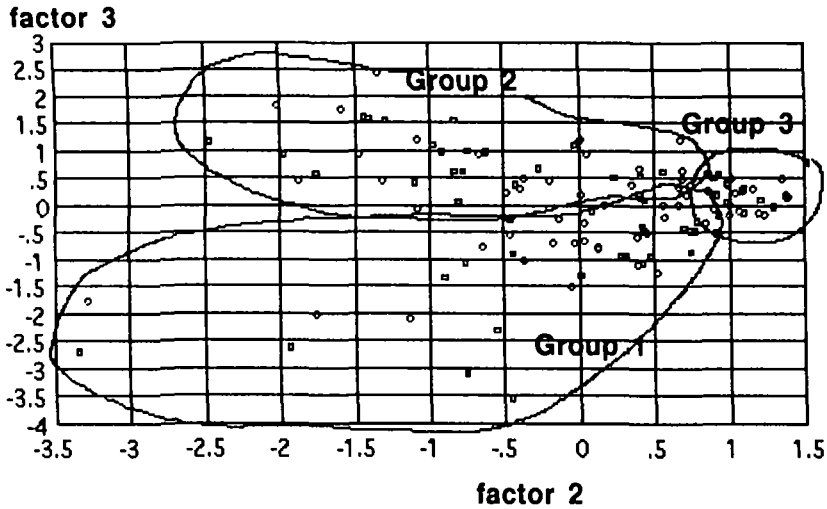

Fig. 4 Plot of the two principal components of the homolog data (Group 1: combustion pattern, Group 2: river sediment, Group 3: lake sediment).

bay areas. In lake sediments, much of the PCDDs and PCDFs were derived from the former use of PCP in the basin. River sediments from northern Japan were characterized by pollution with pesticide-derived dioxins: 1,3,6,8- and 1,3,7,9-TCDD which may be derived from chlorinated diphenyl ether herbicides. The intensity of factor 3 was in good agreement with the use of these pesticides in that area.

Conclusions

Pollution of Japanese aquatic environments with chlorinated dioxins falls into three major groups: pollution from urban and industrialized areas, and pollution with two types of agrochemicals. The latter two sources are already either banned or controlled, and only the urban and industrial sources remained to be regulated.

References

1) Office of Health Studies, Environment Agency (1989 - 1993): Chemicals in the Environment (in Japanese) FY 1989 - FY 1993

2) Yamamoto, T. and M. Fukushima (1993) Modeling study on contribution of combustion source complex to PCDD/PCDF levels in urban air: Chemosphere 27, 295-300