CORRELATION OF DIOXIN CONCENTRATIONS BETWEEN AMBIENT AIR AND PINE NEEDLE IN JAPAN 4

-CATEGORIZATION OF CONGENER PATTERN-

Komichi Ikeda[1], Teiichi Aoyama[2], Atsushi Takatori[3], Hideaki Miyata[4],

Environmental Research Institute Inc., Tokyo Japan [1-3], Food Hygiene Laboratory, Faculty of Pharmaceutical Sciences, Setsunan University, Osaka Japan [4]

Introduction

In this study we have analyzed the congener patterns of PCDDs and PCDFs (hereafter abbreviated as D/F) of totally 107 pine needle samples from west Japan (Kyushu and Chugoku area) sampled in 2 consecutive years of 1999 and 2000. We have categorized the congener pattern of D/F by applying the cluster analysis. Then, we have investigated about the relationship between the source location and the sampling areas of pine needles. Consequently, we found that in the targeted west Japan area, there are 3 typical congener patterns corresponding to the 3 types of sampling area; (1) incineration area, (2) municipal area and (3) background area.

Method

The sampling period of the pine needle was October to November of 1999 and August to September in 2000 carried out by participation and cooperation of the local citizens in the west Japan areas. The target needles of 2 years old were sampled at ca. 1.5m height above the ground level. The number of obtained samples was 51 in 1999 and 56 in 2000 at same target areas, respectively. Those pine needles sampled from the several scattered points were blended into one representative sample of the target area. The target area was categorized into the following three types of area, as partly shown in Fig 1.

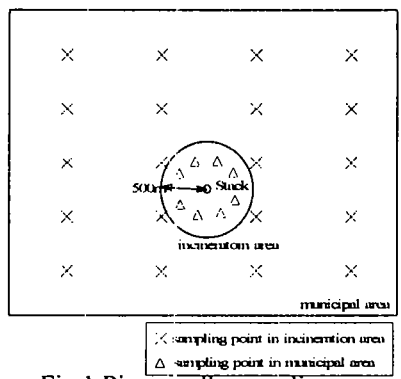


Fig.1 Pine needle sampling area

(1) Incineration Area: Pine needles were sampled at areas adjacent to a certain incinerator.

(2) Municipal Area: Pine needles were sampled within a target area-wide municipal area where some incinerators were under operation.

(3) Background Area: Pine needles were sampled in the area where no active incinerators existed (e.g. areas with no active incinerators or areas with a long distance from municipal areas).

The number of sampling points was set 3 to 6 for each incineration target area, and 10 to 33 for each municipal and background target areas. The applied analytical methodology of D/F was the same method developed by Miyata Laboratory of Setsunan University[1]. Then, we have used the cluster

analysis methodology to determine the D/F congener pattern of 107 samples. For the cluster analysis, the ratio of each congener (Tetra to Octa D/F) in the total D/F concentration was used for data matrix. In this case, the matrix was not necessarily normalized because the units of all the related attribution were the same with each other. After categorizing the congener patters, we have analyzed the change of congener pattern at different sampling areas in both years of 1999 and 2000, in order to find out the correlation between the congener pattern and the type of sampling area.

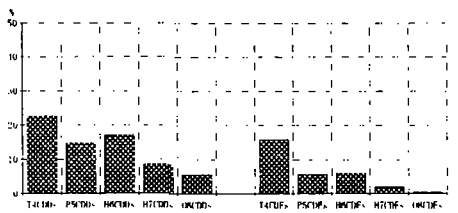
Table 1. Number of samples categorized by cluster analysis

FY of Analysis	Number of samples categorized											
	A	B	C	D	E	F	G	H	I	J	K	L	Total
1999	1	1	1			3	6	6	7	2	15	9	51
2000				1	1		7	6	12	3	7	19	56
Total	1	1	1	1	1	3	13	12	19	5	22	28	107

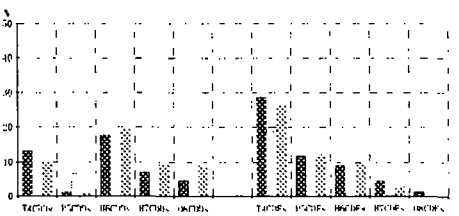
Results and Discussion

The congener patterns of the 107 pine needle D/F concentration were categorized into 12 clusters (A-L) by cluster analysis as shown in Table 1. Figure 2 shows the typical congener pattern of each categorized cluster. Then, we tried to examine the relationship between the type of samping area and the location of pollution sources (incinerators) on the supposition that the characteristics of each different congener pattern could be explained by that relationship. Table 2 presemts the categorized case for 107 samples, showing the obvious pattern alteration to occur during a period of 1999 to 2000.

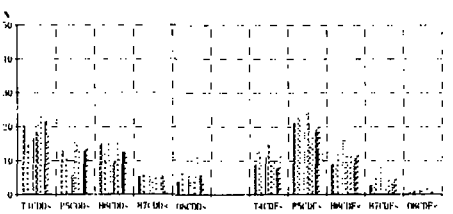
Category B



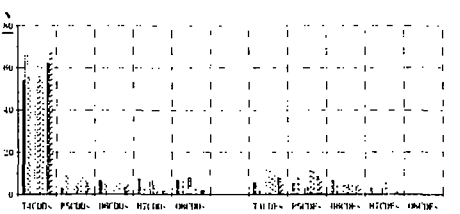
Category F



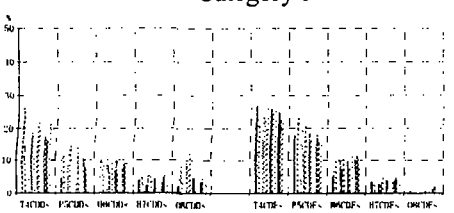
Category G



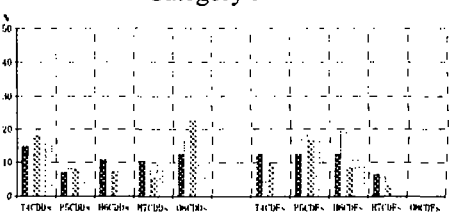
Category H



Category I



Category J



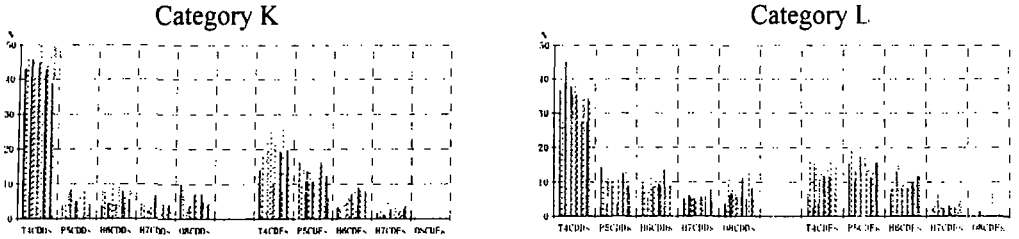


Figure 2 Major congener pattern categorized by cluster analysis

The congener pattern of sample No.1 changed from category I to H. In this case, the pine needle was sampled at a point adjacent to a incinerator in the both years. In 2000, however, the sampling was caried out at a period of a time passing more than one year since the since the incinerator had closed its operation. Therefore, it is possible to say that the sample in 1999 was much more affected by the ambient air D/F pollution than dtd the sample in 2000. On the contrary, Sample Nos.2-5 were the typical cases of the sampling area with a change of municipal area (1999) to incineration area (2000). Most samples having Categories G and I were obtained at the incineration area or the municipal area with a high averag level of air D/F pollution.

Table 2. Cases of congener pattern alteration by conditional changes

Target Areas (municipals)		FY1999		FY2000	
		Pattern	Area and condition	Pattern	Area and condition
No.1	Chikuho Town	I	under operation	H	Closed
No.2	Kanoya City	H	Municipal area	G	Incineration area
No.3	Kagoshima City north area	K	Municipal area	I	Incineration area
No.4	Chikushino City	L	Municipal area	I	Incineration area
No.5	Tagawa City & County	B	Municipal area	I	Incineration area

As shown in Table 2, the congener pattern of categories H, K, L and B were the samples taken from municipal area or from the area where incinerators had already stopped their operation. Three (H, K and L) of these 4 patterns had the common characteristics each other showing the contribution of TCDDs to be extremely. On the other hand, the characteristic pattern of the incineration area was I and G which were also quite similar with each other from the cluster analysis. The sampling areas categorized in the patterns H, K and L could be characterized as the municipal areas or the areas without any specific emission sources (rural area). They might be called as so called background area. As a results, it is possible to refer that the areas of pattern H, K and L with a high concentration of TCDDs is grouped as background area, whereas the area of pattern I and G is did as the are area affected strongly by the activity of waste incinerator.

Then, we have categorized the patterns D, H, K and L as "Background area pattern", and pattens of B, F, G, I and J as "Areas adjacent to incinerator". To verify this hypothesis, we listed all the samples in Table 3 showing the typical pattern alteration. All these were target areas where

the samples of which the congener patter had changed from the pattern of "Areas adjacent to incinerator" to that of "Background area" vice versa. As shown in Table 3, seven of eight areas shifted from the pattern of "Areas adjacent to incinerator" to the pattern of "Background area" and five of six ones did from the pattern of "Background area" to that of "Areas adjacent to incinerator". Thus, the pollution shift on 12 (86%) of 14 target areas was revealed on the basis of our newly developed category method.

Table 3. Congener pattern alteration and concentration change

Types of Pattern alteration	Target Area of samples	D/F conc.[pg-TEQ/g]		Verification of pattern alteration
		1999	2000	
Incineratoin Area to Background area	Fukuoka Pref. Chikuho Town	5.43	0.61	Verified
	Fukuoka Pref. Fukuma Town	2.84	1.52	Verified
	Fukuoka City, Sawara W.	0.79	0.51	Verified
	Fukuoka Pref. Tagawa City & County	1.44	1.10	Verified
	Saga Pref. Saga City	2.89	2.34	Verified
	Yamaguchi Pref. South	1.57	0.73	Verified
	Nagasaki Pref. South east	2.45	0.92	Verified
	Fukuoka City, Higashi W.	1.24	2.38	-
Background area to Incineration area	Kagoshima Pref. Kanoya City	0.40	0.87	Verified
	Oita Pref. Nakatsu City	1.14	1.57	Verified
	Kitakyushu City, Kokurakita W.	0.70	1.32	Verified
	Kagoshima Pref. Kagoshima City North	0.83	1.24	Verified
	Fukuoka Pref. Chikushino City	1.86	3.51	Verified
	Yamaguchi Pref. Shunan area	0.71	0.59	-

Note : "Verified" are areas where both congener pattern and concentration have changed according to the hypothesis.

"-" are areas where the change of congener patter and the concentration were incoherence to our hypothesis.

Acknowledgment

This project has been supported by the participants and organizations of the Executive Committee of Citizen Participatory Monitoring for Dioxin Concentration in Pine Needles. The authors thank to the members Setsunan University, Faculty of Pharmaceutical and staffs Environmental Science Dept. of Maxxam Analytics Inc. to analyze the pine needle samples.

References

1.Masaru Ikeda, Hideaki Miyata, (1997) Time Trend on Accumulation of PCDDs, PCDFs and Co-PCBs in Young Pine Needle (Thesis), Setsunan Univ.