DEVELOPMENT OF SIMPLE AND ACURATE EVALUATION METHOD ON AIR POLLUTION BY DIOXIN ANALOGUES USING JAPANESE BLACK PINE NEEDLE AS AN INDICATOR

Hideaki Miyata[1], Naoki Iwata[2], Teruyuki Nakao[1], Osamu Aozasa[1], Akio Simamura[3] and Souichi Ohta[1]

[1]Faculty of Pharmaceutical Sciences, Setsunan University, 45-1, Nagaotoge-cho, Hirakata, Osaka, 573-0101, Japan

[2]Shimadzu-Techno-Research, Inc., 2-4, Nishinokyo, Sanjyo, Bocho, Nakagyo-ku, Kyoto, 604-8435, Japan

[3]Sibata Scientific Technology LTD, 1-25, Ikenohata 3-chome, Taito-ku, Tokyo, 110-870, Japan

Introduction

In Japan, more than 90% of dioxin analogues including PCDDs, PCDFs and Co-PCBs are released through the flue gas from several thousands municipal solid waste and industrial waste incinerators. The total annual emission in the fiscal year of 1999 was estimated to be ca. 3,000 gTEQ. The amount was remarkably larger than those of European countries. Therefore, in recent year, there is a much concern to the air pollution. In Japanese official method, 1000m^3 of atmospheric air is sampled for 24 hrs. using a high-volume air sampler or for 1 week using a low- volume air sampler, and then analyzed for dioxin analogues. In general, the frequency of air pollution survey is only 2 or 4 times per year, due to an extremely high cost with ca. 300,000 yen for one survey at the commercial base. However, we had already revealed the air pollution level was in a great time alteration with a several tens times within a year[1)]. Taking these facts into consideration, it is emphasized that the real situation of air pollution level in Japan is obscure. From thus point of view, in this study, we tried to develop a simple, accurate and economic evaluation method for the air pollution by dioxin analogues using Japanese black pine needle as an indicator.

Materials and Methods

Sample

The air sampling was performed during a period of August 2000 to October 2001 on the campus of Setsunan University, Hirakata, Osaka, Japan. We got 50 air samples of continuous 7days collection using a newly developed low-volume air sampler with the flow rate of 40 L/min. The sampler possessed a glass fiber filter (GFF) for collection of particle phase dioxin analogues and two polyurethane from plugs (PFU) of vapor phase ones. On the other hand, the Japanese black pine needle sample was weekly obtained during the same period and at the same sampling point to the case of air sample.

Analytical method

The air sample was cleaned up for dioxin analogues according to our previous methods[1)]. The outline was essentially composed of an addition of internal standards, extraction with toluene (for collection on GFF) and acetone (for collection on PUF) for 5hrs. under reflux, combine of two extracts, and cleaning up on a multi-layer silica gel column and an alumina column. On the other hand, the pine needle was analyzed according to our previous method[2)]. The outline was consisted of an addition of internal standards, extraction with toluene for 5 hrs. under reflux, removal of chlorophyll by silica gel,

and cleaning up on a multi-layer silica gel column and an alumina column. The cleaned up extract from air sample or pine needle sample was analyzed for dioxin analogues in EI-SIM mode at a resolution of 10,000 using a Hewlett Packard 5890J gas chromatograph-JEOL M700 mass spectrometer. A calculation of TEQ of the dioxin analogues in analyzed samples was carried out on the basis of TEFs by WHO.

Results and Discussion

As already described, the real situation of air pollution by dioxin analogues in Japan has been obscure until today. Therefore, we tried to make clear the air pollution using our newly developed low-volume air sampler. In this study, we obtained 50 air samples of continuous 7 days collection during a long period of August 2000 to October 2001 on the campus of Setsunan University. Consequently, it was first revealed the real situation of air pollution by dioxin analogues. The average weekly air pollution level was 19.7 pg/m^3 with the minimum of 9.62 pg/m^3 and the maximum of 37.1 pg/m^3 (Fig. 1). There was observed a great time alteration of the ratio of vapor phase to the total in this experimental period. The ratio showed ca. 80 % in the hot summer season, whereas only ca. 20 % in the cold winter season. Especially, the lower chlorinated dioxin analogues such as tetra- and penta-chlorinated congeners occupied the most of vapor phase. Thus, the existence state of dioxin analogues changed in connection with the atmospheric temperature. As shown in Fig. 2, there was a good positive correlation with the formula (1) between the vapor phase ratio (%) and the air temperature. The coefficient of correlation (R^2) in 16 samples number was 0.9012.

Vapor ratio (%) = 2.1963 x [Air temperature (°C)] + 16.945 —— (1)

As above described, we obtained weekly the pine needle sample during the same period and at the same area to the case of air sample. From the analytical data of the pine needle sample, the accumulation level of dioxin analogues in the needle was found to relate closely to the needle age. The correlation was shown in the formula (2). The coefficient of correlation (R^2) in 50 samples number was 0.8444 (Fig. 3).

Accumulation level of dioxin analogues (pg/g) = 56.05 x [Needle age (month)] —— (2)

We had already revealed that the dioxin analogues in the vapor phase accumulated mainly in the pine needle. Therefore, we examined the correlation between the average monthly level in the vapor phase and the accumulation level in the needle, resulting in to get the following formula (3). The coefficient of correlation (R^2) in 16 samples number was 0.6013 (Fig. 4).

Average monthly level in vapor phase (pg/m^3) =

0.1852 x [Accumulation level in pine needle (pg/g)] —— (3)

As shown in Fig. 5, there was a good positive correlation between the actual concentration and the TEQ concentration of dioxin analogues in the air. The coefficient of correlation (R^2) in 27 samples number was 0.7282 (Fig. 5).

The conversion formula of the TEQ level from the actual level was shown in the formula (4).

TEQ level (pgTEQ/m^3) in the air = 0.0107 x [Actual level (pg/m^3) in the air

From results, we established a simple and accurate evaluation method for the TEQ level of dioxin analogues in the air on the basis of the actual level in the pine needle. The evaluation expression was as follows.

$$\text{TEQ level in the air (pgTEQ/m}^3\text{)} = \frac{\text{[Actual level in the pine needle (pg/g)]} \times 0.1852 \times 100 \times 0.0107}{\text{[Needle age (month)]} \times \text{[Average monthly vapor phase ratio in the air (\%)]}}$$

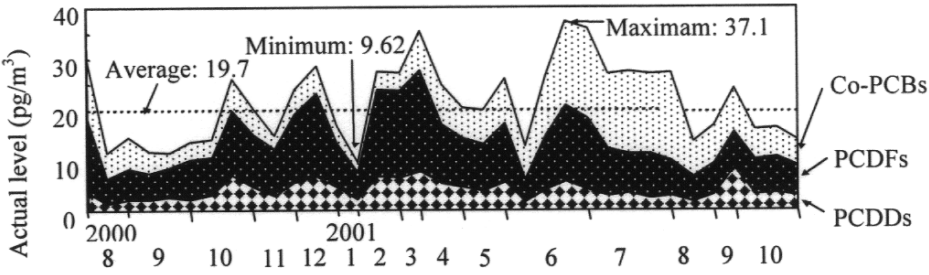

Fig. 1. Weekly alteration of air pollution levels by dioxin analogues

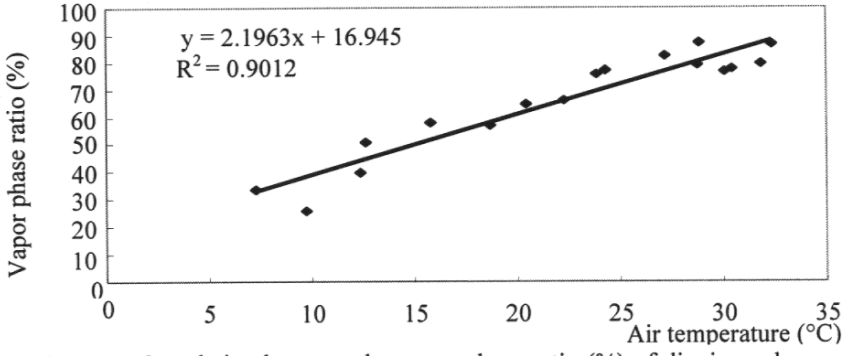

Fig. 2. Correlation between the vapor phase ratio (%) of dioxin analogues and the air temperature

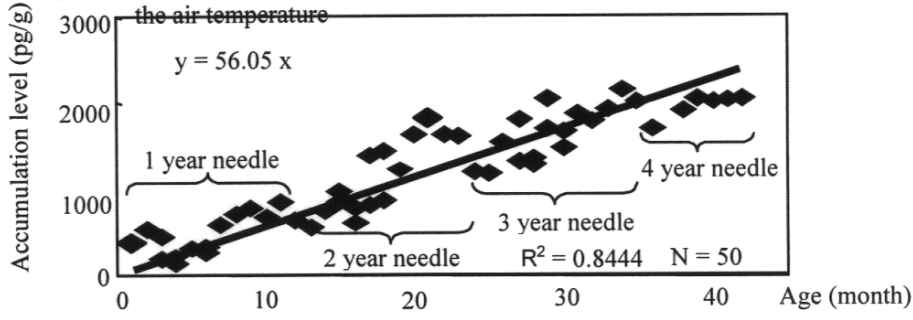

Fig. 3. Correlation between the accumulation level of dioxin analogues and the age in the pine needle

Using this evaluation method, the air pollution levels were estimated on the basis of the data in the pine needle in 8 areas in Osaka Prefecture. As shown in Table 1, the evaluated TEQ level was gave a good coincidence with the actual analytical TEQ level.

References

1. Miyata, H., Takamitu, S., Iwata, N., Nakao, T., Aozasa, O., Ohta, S.. (2000) Organohalogen Compounds, 46, 373
2. Miyata, H., Takamitu, S., Iwata, N., Nakao, T., Aozasa, O., Ohta, S.. (1999) Organohalogen Compounds,43,2

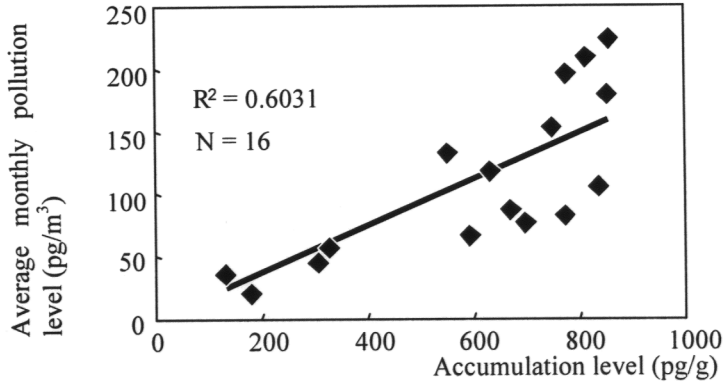

Fig. 4. Correlation between the average monthly pollution level in the air and the accumulation level in the pine needle

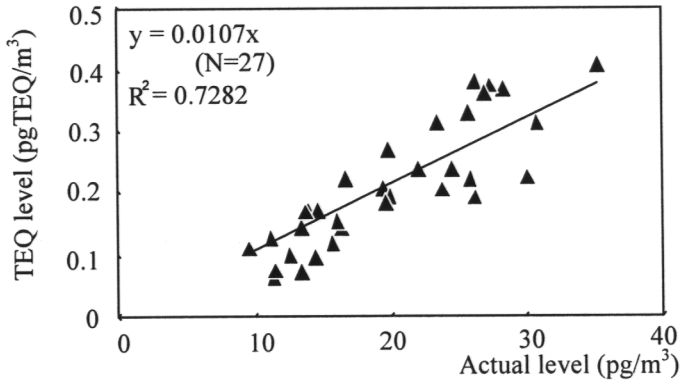

Fig. 5. Correlation between the actual level and the TEQ level of dioxin analogue in the air

Table 1. Comparison of the actual analytical TEQ level and the evaluated TEQ level of dioxin analogues in the air at 8 areas

Pollution level in the air	Control area		Area close to sources			Urban area		
Actual analytical level (pgTEQ/m^3)	0.070	0.15	0.075	0.074	0.29	0.21	0.39	0.21
This evaluated level (pgTEQ/m^3)	0.10	0.095	0.085	0.11	0.26	0.22	0.21	0.19