INVESTIGATION ON ASSESSMENT OF AIR POLLUTION BY DIOXIN ANALOGUES USING JAPANESE BLACK PINE NEEDLE AS AN INDICATOR

Hideaki Miyata, Sigekazu Takamitsu[1], Naoki Iwata, Teruyuki Nakao, Osamu Aozasa and Souichi Ohta

Faculty of Pharmaceutical Sciences, Setsunan University, 45-1, Nagaotoge-cho, Hirakata, Osaka, 573-0101, Japan
[1] Oil Division, Product Development Group, Kansai Tech Co., 3-1-176, Fukusaki, Minato, Osaka 552-0013, Japan

Introduction

In Japan, more than 90% of dioxin analogues including polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and coplanar PCBs (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 1998 was estimated to be ca. 3,000 gTEQ. The amount was remarkably larger than those of foreign countries such as Germany, Sweden and Netherlands etc. Consequently, the air pollution level in Japan was more than ten times greater compared to many foreign countries.Therefore, in recent years in Japan, there is a much concern to air pollution by dioxin analogues.

Now, in Japanese official method, 1000 m^3 of atmospheric air is sampled for 24 hrs. using a high volume air sampler, and then analyzed for dioxin analogues. In general, the air pollution survey has been carried out at a rate of 2 or 4 times per year. However, the 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.

The indeciduous Japanese black pine tree grows in the whole area of Japan except for Okinawa (the most southern prefecture of Japan), and its needle has the lipophil cuticle on the surface. In 1997, we found the pine needle was a suitable biomonitoring indicator for the survey of average air pollution by dioxin analogue[2)]. Therefore, in this study, we tried to investigate a relationship of the pollution level between pine needle and ambient air at two locations in Osaka, the second big prefecture of Japan.

Experiments

1) Ambient air and Japanese black pine needle samples

Sampling was performed in September of 1998 to November of 1999 on the campus of Setsunan University and in September of 1998 to November of 1999 at Wani Park, northern Hirakata, Osaka, Japan. The sampling points are respectively located at a distance of 20 km and 16 km on the north direction from a central part of Osaka, one of the represent urban regions of Japan. The ambient air sample was collected using a high volume air sampler equipped with a glass fiber filter (GFF) for collection of particulate phase compounds and two polyurethane form plugs (PUF) for collection of gas phase compounds. The detail was described eleswhere[1)]. The number of samples collected during this experimental period was 51 at Setsunan University and 43 at Wani Park. On the other hand, Japanese black pine needle was also weekly sampled at the same two points. 49 and 41 samples were respectively obtained at Setsunan University and at Wani Park.

2) Analytical method:

Air sample and pine needle sample was respectively cleaned up for dioxin analogues according to our previous methods[1,3]. The outline was essentially composed of addition of internal standards, extraction with toluene or acetone for 5 hrs. under reflux, removal of chlorophyll by silica gel (for pine needle), multi-layer silica gel column chromatography and alumina column chromatography. The treated sample solution was analyzed in EI-SIM mode at a resolution of 10,000 using a Hewlett Packard 5890J GC-JEOL M700 MS. A calculation of 2,3,7,8-TCDD toxicity equivalency quantity (TEQ) of dioxin analogues in analyzed samples was carried out on the basis of TEFs by WHO[4].

Results and discussion

As shown in Table 1, the concentration of dioxin analogues in 43 ambient air samples from Wani Park was in a wide range of 0.0033 pgTEQ/m^3 to 1.19 pgTEQ/m^3 with the average of 0.408 pgTEQ/m^3. The ratio of maximum versus minimum showed a big figure of 36.1.

Table 1. Pollution levels of dioxin analogues in ambient air and Japanese black pine needle from two points in Hiraka, northern Osaka

Location	Sample	No. of Sample	Pollution level (pgTEQ/m^{3*}, pgTEQ/g dry weight**)			Ratio***
			Minimum	Maximum	Mean	
Wani Park	Air	43	0.033	1.19	0.408	36.1
	Pine needle	41	7.40	30.5	18.3	4.1
Setsunan Univ.	Air	51	0.038	2.50	0.535	65.8
	Pine needle	49	7.19	34.2	13.6	4.8

*: For air sample **: For pine needle ***: Ratio of maximum level versus minimum level

The similar observation was also seen in 51 air samples from a sampling point at Setsunan University. The minimum, maximum and average levels were 0.038, 2.5 and 0.535 pgTEQ/m^3, showing the minimum/maximum ratio to be 65.8. Thus, even in the weekly survey, the pollution level of dioxin analogues in ambient air changed more than several tens times at the maximum during a period of ca. a year. This result indicates that the time alteration in the consecutive daily survey for a year will be much more greater. In fact, in this year, the survey of consecutive daily analyses for three months at three points in Kanagawa Prefecture, middle Japan, gave a great time alteration with a maximum/minimum ratio of 50 to 600. This again insists that the daily pollution alteration will exceed more than 100 times at the maximum.

In this study, it was revealed that the pollution level of ambient air had no correlation with the whether conditions such as wind velocity and humidity. If an emission amount of dioxin analogues from the sources is constant, the ambient air pollution level has to change in a good correlation with a magnitude of wind velocity. From these things, it is surmised that the emission level from sources might greatly change moment by moment. In addition, the air pollution level

of dioxin analogues was decreased at a rate of ca. 50% by rain, due to mainly a decrease of dioxins in the particle phase (dioxin analogues absorbed on GFF). The effect continued by the following day.

On the other hand, compared to ambient air samples, Japanese black pine needle samples from Wani Park showed ca. nine times smaller time alteration of pollution level, showing the maximum/minimum ratio to be only 4.1 (Table 1). The minimum, maximum and average levels were respectively 7.40, 30.5 and 18.3 pgTEQ/g dry weight.

The pine trees in Setsunan University were all half-breed of Japanese black pine and red pine trees. In this case, the pine needle gave noticeably a smaller time alteration of pollution level than did ambient air. The ratio of maximum level/minimum level for 15 months was only 4.8, showing the ratio to be equivalent to a fifteenth of that of ambient air.

In this study, at both sampling points of Wani Park and Setsunan University, there was also observed a positive good correlation of the pollution level between pine needle and ambient air with a time lag of ca. three months. This result indicates that the accumulation level in the pine needle is reflected in the average pollution level of ambient air with a time lag of ca. three months. Therefore, we calculated a ratio of pollution level between pine needle and ambient air with a time lag of three months, in order to estimate the average level of ambient air from the level of pine needle.

The pollution ratio of black pine needle versus ambient air at Wani Park showed a seasonal variation (Table 2). The summer season gave the highest ratio of 64.2, whereas the winter season

Table 2. Correlation of pollution level between pine needle and ambient air with a time lag of three months (Sampling point: Wani Park)

Sample	Ambient air ($pgTEQ/m^3$)	Pine needle (pgTEQ/g dry weight)	Ratio of Pine needle/Air
Sampling Period	98.11 – 98.12	99.1 – 99.3	36.3
Average level	0.560	20.3	
Sampling Period	99.1 – 99.2	99.4-99.5	33.7
Average level	0.555	18.7	
Sampling Period	99.3 – 99.5	99.6 – 99.8	53.2
Average level	0.344	18.3	
Sampling Period	99.6 – 99.8	99.9 – 99.11	64.2
Average level	0.229	14.7	

Table 3. Correlation of pollution level between pine needle and ambient air with a time lag of three months (Sampling point: Setsunan University)

Sample	Ambient air ($pgTEQ/m^3$)	Pine needle (pgTEQ/g dry weight)	Ratio of Pine needle/Air

Sampling Period	98.10 – 98.12	99.1 – 99.3	18.4
Average level	1.00	18.4	
Sampling Period	99.1 – 99.2	99.4-99.5	27.7
Average level	0.422	11.7	
Sampling Period	99.3 – 99.5	99.6 – 99.8	34.5
Average level	0.330	11.4	
Sampling Period	99.6 – 99.8	99.9 – 99.11	60.0
Average level	0.220	13.2	

did the smallest ratio of 33.7. In the summer season, most dioxin analogues were present in the vapor phase (dioxin analogues absorbed on PUF). In addition, the congener profile of dioxin analogues in the pine needle was similar to that in the vapor phase. From these results, it is surmised that dioxin analogues in pine needle might be mainly derived from the vapor phase. The speculation can give a good explain of this results.

The half-breed pine needle samples from Setsunan University gave also a similar seasonal accumulation tendency (Table 3). However, compared to the Japanese black pine samples (see Table 1), they had a noticeably smaller uptake rate of dioxin analogues from the air during this experimental period except for summer season.

This indicates that the uptake rate of dioxin analogues from air is different in a kind of pine tree. In this study, consecutive weekly analyses were carried out in order to survey a real situation of the air pollution. However, for the aim, the number of trials was not enough. Hereafter, we will try to practice consecutive daily air determinations in order to develop a simple and accurate assessment method for air pollution using black pine needle as an indicator.

Literature cited

1. Miyata, H., Takamitsu. S., Nakao, T., Aozasa, O., Ohta, S. (**1999**) Organohalogen Compounds, 43, 203
2. Miyata, H., Nakao, T., Aozasa, O., Ohta, S., Ikeda, M. (**1997**) Organohalogen Compounds, 32, 130
3. Nakao, T., Aozasa, O., Ohta, S., Miyata, H. (**1998**) Organohalogen Compounds, 39, 347
4. Van den Berg, M., Birnbaum, L., Bosveld, A., Brustrom, B., Cook, P., Freeley, M. (**1998**) Environ. Health Persp., 106, 775