ACCURATE EVALUATION OF AIR POLLUTION BY DIOXIN ANALOGUES USING A NEWLY DEVELOPED LOW-VOLUME AIR SAMPLER

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

Faculty of Pharmaceutical Sciences, Setsunan University, 45-1, Nagaotoge-cho, Hirakata, Osaka, 573-0101, Japan
[1] Sibata Scientific Technology LTD, 1-25,Ikenohata 3-chome, Taito-ku, Tokyo, 110-870, Japan

Introduction

Recently, dioxin analogues including polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and coplanar PCBs (Co-PCBs) are wide spread persistent contaminants, which are turned into a grave international issue. Especially, in Japanese is the biggest waste burning-up country in the world. Hence their quantity which is discharged into the environment is supposed to be the highest level. The total annual emission in the fiscal year of 1998 was estimated to be ca. 3,000 gTEQ. Consequently, the air pollution level in Japan was more than ten times greater compared to many foreign countries. Therefore, in recent year in Japan, there is a much concern to air pollution by dioxin analogues.

Now, in Japanese official method, 1000m^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 oh 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.

Then, there was a report concerning air pollution by dioxin analogues that the condition of weather etc. sharp fluctuation a daily. Therefore, in this study, we tried to construct the air pollution method, which can be made to reduce an influence by the weather condition etc., using an air sample during a period of 1 week to 1 month obtained.

Experiments

1) Analysis samples:

The sampling for the short time experiment was performed during a period of on July 5th to 11th of 2001 on the campus of Setsunan University, Hirakata, Osaka, Japan. We got one sample of continuous 7days collecting using a newly developed low-volume air sampler with the flow rate of 40 L/min, and 7 samples of daily collecting for 24 hrs. using the high-volume air sampler with the flow rate of 700 L/min. The both samplers possessed a glass fiber filter (GFF) for collection of particlation phase compounds and two polyurethane from plug gas phase compounds.

The sampling for the long time experiment was carried out during a period of July of 2000 to February of 2001 on the same sampling point. During the period, we obtained 20 ambient air samples of continuous 7days collecting using the low-volume air sampler with the flow rate of 40 L/min.

2) Analytical method:

Analysis sample was cleaned up for dioxin analogues according to our previous methods[1]. The outline was essentially composed of addition of internal standards, extraction with toluene or acetone for 5hrs. under reflux, refined by multi-layer silica gel column chromatography and

alumina column chromatography. The cleaned up extract 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 2,3,7,8-TCDD toxicity equivalency quantity (TEQ) of the dioxin analogues in analyzed samples was carried out on the basis of TEFs by WHO[2].

Results and discussion

1) Short time experiment

As already described in the sampling for the short time experiment, we got 7 air samples of daily collecting for 24 hrs. using the high-volume air sampler on the campus of Setsunan University. Figure 1 illustrates the daily alteration of dioxin analogues in gas phase (PUF) and particle phase (GFF). As shown in Table 1 and 2, there was a great discrepancy in their pollution level of both phases, showing the level to be in a wide range of 4.02 to 23.2 pg/m^3 for gas phase with the average of 14.2 pg/m^3, and 1.39 to 10.1 pg/m^3 for particle phase with the average of 5.59 pg/m^3. On July 7th, the weather condition was cloudy and rainy. The pollution level of dioxin analogues was the lowest during the examined period. In addition, the level was the second lowest in the following day of June 8th. From this result, it was revealed that the rainfall gave a strong decrease of the atmospheric pollution level for dioxin analogues on the rainy day and the following day (Table 1 and 2). The decline ratio of atmospheric suspension particle was greater during 7th to 8th than 6th to 7th, whereas the decline ratios of dioxin analogues in gas and particle phases was smaller during 7th to 8th than 6th to 7th. That is, there was a discrepancy in the decrease tendency of the suspension particle and dioxin analogues. It is well known that the size of suspension particle becomes smaller, and the level of pollutants in particle per unit weight becomes greater. In addition, the larger particle is more effectively fallen on the ground by rain than did the smaller one and pollutants of gas phase. Therefore, the above discrepancy of decrease rate was surmised to come from the difference in the drop rare among larger suspension particle, smaller suspension one and gas phase matter.

In this experimental period, the total level of particle and gas phases was in a wide range of 1.24 to 7.41 pg/m^3 for PCDDs, 3.77 to 22.7 pg/m^3 for PCDFs and 0.40 to 3.37 pg/m^3 for Co-PCBs and 5.42 to 33.4 pg/m^3 for the total, respectively (Table 1). The ratio of maximum/minimum level was 6.0 for PCDDs, 6.0 for PCDFs, 8.4 for Co-PCBs and 6.2 for the total, respectively. Thus, the daily air pollution level was found to fluctuate with a change of weather condition etc.

As shown in Table 1 and 2, the average level of dioxin analogues in gas and particle phase for 7 days using the high-volume air sampler were 4.91 pg/m^3 for PCDDs, 12.7 pg/m^3 for PCDFs, 2.13 pg/m^3 for Co-PCBs, 19.7 pg/m^3 for the total, respectively. These levels were well coincident with their respective ones in an air sample obtained from the low-volume air sampler, showing the level to be 4.91 pg/m^3 for PCDDs, 12.3 pg/m^3 for PCDFs, 2.36 pg/m^3 for Co-PCBs, 19.6 pg/m^3 for the total, respectively. The difference of the latter versus the former was only 0.0% for PCDDs, 3.1% for PCDFs, -10.8% for Co-PCBs, 0.51% for the total, respectively. From this experimental, our newly developed low-volume air sampler was confirmed to be a suitable sampling machine for the determination of average dioxin analogues in atmosphere during a rather long time of 7 days.

2) Long time experiment

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 long time experiment, we obtained 20 air samples of continuous 7 days collecting on the campus of Setsunan University. During the experimental period of July of 2000 to February of 2001, the average whole weekly air pollution levels were

made clear as 4.54 pg/m^3 for PCDDs, 11.6 pg/m^3 for PCDFs, 1.11 pg/m^3 for Co-PCBs and 17.2 pg/m^3 for the total (Fig 1). As judged in this data, the major pollutant was PCDFs with a contribution of 67.2 % to the total, and the second and the third contributors were PCDDs with 26.4 % and Co-PCBs with 6.46 %, respectively . From this result, it was confirmed that the air pollution in Hirakata was mainly derived from the waste combustion facility, because the contribution pattern was a typical emission pattern for the dioxin analogues from the waste combustion facility. In addition, compared to as our expectation, it was also found that the weekly alterations of their pollution levels were smaller, resulting in the level to be in a range of 1.45 to 7.63 pg/m^3 for PCDDs, 4.92 to 20.8 pg/m^3 for PCDFs, 0.30 to 2.30 pg/m^3 for Co-PCBs and 6.90 to 30.88 pg/m^3 for the total. In other words, the ratios of the maximum / minimum were only 5.3 for PCDDs, 4.2 for PCDFs, 7.7 for Co-PCBs and 4.4 for the total, respectively. Within a month, the fluctuation became smaller. For example, in August, the total levels of 4 air samples were 22.1, 19.8, 6.98 and 9.03 pg/m^3, indicating the maximum/minimum ratio to be only 3.2. In a case of each dioxin analogues, the range was 1.45 to 4.00 pg/m^3 with a maximum/minimum ratio of 2.8 for PCDDs, 4.92 to 16.0 pg/m^3 with 3.3 for PCDFs and 0.58 to 2.11 pg/m^3 with 4.2 for Co-PCBs, respectively.

The weekly composition variation of the pollutants was observed to be not stable, in which the composition ratio was 18.1 to 32.9 % for PCDDs, 61.8 to 74.6 % for PCDFs and 2.87 to 12.0 % for Co-PCBs, respectively. Especially, the fluctuation of Co-PCBs was bigger than other two pollutants. This phenomenon was considered to reflect the emission pattern of dioxin analogues from the incinerator due to its unstable content of combustion waste.

Compared to the case of the actual concentration, the weekly total TEQ of dioxin analogues had a greater alteration with a range of 0.07 to 0.37 pgTEQ/m3 (Fig. 1). The ratio of the maximum/minimum was 5.11 and was bigger in comparison with the case (4.4) of the actual concentration. Especially, the degree of the alteration was bigger in PCDDs with a ratio of 7.62 and PCDFs with 8.40 than Co-PCBs with 4.75.

As well as the of the actual concentration, the contribution of each dioxin analogue to the total TEQ was found to be almost equal, showing the average to be 29.6 % for PCDDs, 63.2 % for PCDFs and 7.25 % for Co-PCBs, respectively. That is, the most effective pollutant among dioxin analogues for humans was revealed to be PCDFs.

From all data in this study, our newly developed low-volume an sampler was an excellent air sampling machine for the judge of a real situation of atmospheric pollution by dioxin analogues. In addition, we could the first reveal the weekly fluctuation for their pollution in Hirakara, Osaka.

Table 1, Comparision of concentration of dioxin analoges in atmospheric gas phase between high volume air sampler and low volume air sampler (pg/m^3)

	High-volume air sampler								Low-volume air sampler
Sampling day	7/4	7/5	7/6	7/7	7/8	7/9	7/10	Mean	7/4-10
PCDDs	4.75	1.49	0.76	1.25	5.09	3.90	3.28	2.93	2.99
PCDFs	10.8	6.06	2.87	3.61	12.9	16.0	11.7	9.16	9.36
Co-PCBs	2.98	2.72	0.38	0.69	1.78	3.28	2.66	2.07	2.28
Total	18.6	10.2	4.02	5.55	19.7	23.2	17.7	14.1	14.6

Table 2, Comparision of concentration of dioxin analoges in atmospheric particle phase between high volum sampler e air and low volume air sampler (pg/m^3)

	High-volume air sampler								Low-volume air sampler
Sampling day	7/4	7/5	7/6	7/7	7/8	7/9	7/10	Mean	7/4-10
PCDFs	2.46	1.24	0.47	0.58	2.32	3.37	3.42	1.98	1.92
PCDFs	4.25	3.28	0.90	0.82	3.07	6.66	5.91	3.56	2.96
Co-PCBs	0.077	0.026	0.020	0.108	0.059	0.096	0.0058	0.056	0.073
Total	6.78	4.54	1.39	1.51	5.45	10.13	9.34	5.59	4.95
Suspension particle (μg/m^3)	50.7	43.3	40.7	22.5	68.9	128	84.6	62.8	68.5

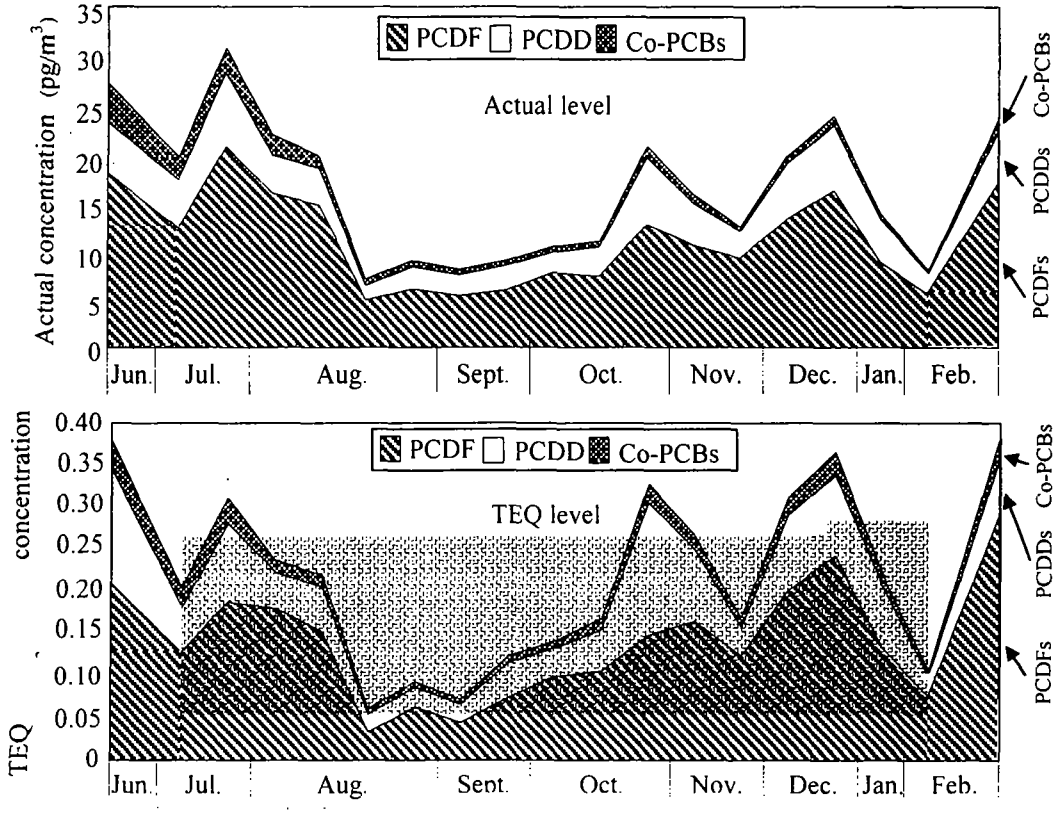

Fig. 1 Fluctuation of dioxin analogous concentration in atmospheric air

References

1. Miyata, H., Takamitu, S., Iwata, N., Nakao, T., Aozasa, O., Ohta, S., (**2000**) Organohalogen Compounds, 46, 373
2. Van den Berg, M., Birnbaum, L., Bosveld, A., Brustrom, B., Cook, P., Freeley, M. (**1998**) Environ. Health Persp., 106, 775