Dioxin Concentration of Particulate and Gaseous Substances in the Ambient Air by Particle Size — Comparison between Specimens Collected in Summer and in Winter at Tokyo —

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Size-fractionated air-borne particles and gaseous samples were collected using Andersen low pressure impactor with polyurethane foam at Tokyo. Dioxin concentrations of these particles and gaseous substances were measured with high resolution gas chromatograph/high resolution mass spectrometer (HRGC/HRMS). Particle diameter distribution has two peaks, one around 0.7 μm and the other around 5 μm both in summer and winter. But, dioxin has a peak at around the particle diameter of 0.52 μm. And, It was observed that smaller particle was the higher weight concentration of dioxins in the particle except in the case of tetrachlorodibenzofurans (TeCDFs). From these results, it was recognized that 75% or more of toxic dioxin component was contained in particles of 1 μm or smaller.

Key words — particle size, dioxin, fine particle

INTRODUCTION

The ambient air contains very small amounts of toxic substances such as dioxin. Those toxic substances exist as gaseous and particulate phase depending on several conditions such as molecular weight or vapor pressure. It has been reported that dioxins are typical air pollutants in recent years and exist both in gaseous and particulate state in the ambient air.¹ The majority of these dioxins are generated by an activity combustion at fixed sources such as waste incineration facilities and discharged in the air. Particles discharged from those sources vary in diameter. We continuously take those substances into our body mainly by breathing. It has been reported that the deposition ratio of such particulate substances on the respiratory tract differs depending on particle size.² Therefore, to examine the exposure status and take measures against these substances, it is very important to study the concentration of these toxic substances in particles by particle size and gaseous phase.

In this research, polyurethane foam was attached to the Andersen sampler with a low-pressure impactor, and particulate substances in the ambient air were collected by particle size in 12 stages with a range of 12.1 μm or larger to 0.13 μm or smaller. The gaseous components were collected on the polyurethane foam, and dioxins contained in those suspended particulate and gaseous specimens were measured by HRGC/HRMS analysis.

MATERIALS AND METHODS

Sampling — Two Andersen samplers with a low-pressure impactor with polyurethane foam (PUF) in an aluminum shelter [TOKYO DYLEC Corporation (Japan) make, Fig. 1] were installed on the rooftop of National Institute of Public Health (Shirokanedai, Minato-ku, Tokyo, Japan). While there are scarcely
any main sources like municipal solid waste incinerator, some big road, national road of route 1, Meguro Street etc., were nearer to sampling location. These two samplers were simultaneously operated and suspended particles and gaseous components were collected with a teflon binder filters (T60A20, 80 mmφ; Pallflex Products Corp. make) by particle size, and with PUF (90 mmφ, 50 mm thickness, density; 0.016 g/cm³), respectively.

Prior to sampling, the teflon binder filter underwent ultrasonic cleaning with acetone and dichloromethane twice each for 10 min. They were then placed in a drying apparatus to warm up to 50°C for an elimination of the cleaning solvent. After the elimination, the filter was left to stand for 24 hr in a desiccator with a keeping a constant humidity of ca. 50%, and then the weight of the filter was measured (initial measurement). Prior to sampling, the PUF was also washed by rubbing with acetone, washed by Soxhlet extraction with acetone, and then dried for 24 hr before use. It was checked at that time that there was no smell of acetone. The ambient air was sucked at a flow rate of 20 l/min. for sample collection. This flow rate was set to –550 mmHg by adjusting the differential pressure of the sampler at the final stage. In order to measure the weight of suspended particles, the sampling was continuously conducted for one week, and then the filter was placed on an aluminum foil and set aside for 24 hr in a desiccator under a constant humidity. After that, the weight of each filter was measured (subsequent measurement). The weight of particles collected for each size-class was calculated on the basis of a difference in weight between the initial and subsequent measurement. These specimens were placed in a polyethylene bag and refrigerated for storage at –80°C until analysis.

**Dioxin Analysis** — On the supposition that dioxin content might be very low, specimens for 19 sets (summer samples) collected during a period of July to September and for 17 sets (winter samples) collected during a period of December to February were used for this study. The average temperatures of sampling periods were 26.1°C for summer and 7.1°C for winter, respectively. These samples were taken out of the refrigerator and set aside until returning to the room temperature. Each size-class filters was extracted with toluene using Soxhlet apparatus in order to extract organic components. Each PUF underwent Soxhlet extraction with toluene, respectively and then extracted liquid was gathered up. The half of extracted liquid specimen from filters and PUF was used for dioxin analysis, and the rest was put in a brown bottle and stored in a refrigerator as spares. In one season, 12 samples from particle and one sample from gaseous were obtained. Thus, both summer and winter, total sample number is 26 specimens. Dioxin analysis of these specimens was conducted as follows according to the documents already issued.3,4) Internal standard substance (cleanup spike) was added to the extracts, multi-layer silica gel column and activated carbon-dispersed silica gel column processing were performed for clean-up step, and then syringe spike was added to the final solution to make samples for GC/MS measurement.

The GC/MS device used was JMS-700 (JOEL Ltd. make), and the measurement was taken under the conditions of resolution of 10000 or higher than 10000 and the ionizing voltage of 38 V. As capillary columns, CP-SIL88 (60 m length, 0.32 mm i.d., 0.1 µm film thickness; SIGMA make) that is capable of analyzing tetrachlorodibenzo-p-dioxins (TeCDDs)/tetrachlorodibenzofurans (TeCDFs) - hexachlorodibenzo-p-dioxins (HxCDDs)/hexachlorodibenzofurans (HxCDFs) and RH-17 (30 m length, 0.32 mm i.d., 0.25 µm film thickness; Inventex make) that is capable of analyzing heptachlorodibenzo-p-dioxins (HpCDDs)/heptachlorodibenzofurans (HpCDFs) - octachlorodibenzo-p-dioxin (OCDD)/octachlorodibenzo furan (OCDF) were used. Measurement conditions were as follows:

When CP-SIL88 capillary column was used;
100°C (1.5 min. Hold)-20°C/min.-180°C-3°C/min.-260°C (25 min. Hold)
When RH-17 capillary column was used:
100°C (1.5 min.Hold)-20°C/min.-180°C-10°C/min.-280°C (10 min.Hold)

As internal standard substances, 2,3,7 and 8 chlorine-substituted 17 isomers were used for dioxin measurement, and the quantity was determined by the internal standard method.

RESULTS AND DISCUSSION

Particle Size Distribution by Mass of Suspended Particles in the Air

By using an Andersen sampler with a low-pressure impactor, the weight of suspended particles collected by size-class was measured once a week, and then particle size distribution by particle weight in unit air (particle mass) was calculated using ad-in software.\(^5\) Figure 2 indicates the diameter distribution of obtained particles with two big peaks of around 0.7 µm (fine particle side) and around 5 µm (coarse particle side) both in summer and winter. However, there was a remarkable difference in the distribution pattern between the summer and winter specimens. In summer specimens, the dimensions of the fine and coarse particle peak were equal each other, whereas the fine particle peak was apparently bigger than the coarse one in the winter specimens. Funasaka, \textit{et al.} measured the particle diameter distribution in automobile exhaust monitoring station and general ambient air monitoring station, and reported that particle size mass-distribution differed depending on individual particle generating source such as automobiles.\(^6\) While particle size mass-distribution also differed in this research, the specimens were collected at the same place. These indicate that particle size distribution per particle concentration differs depending on not only the places and the sources but also the season.

Concentration of Dioxins in the Air by Particle Size

Dioxin and dibenzofuran homologues in the specimens collected on the basis air suspended particle size in summer and winter seasons were measured, and the concentration of each homologue per unit air quantity was calculated. Fig. 3 and Table 1 indicate the concentration of dioxin and dibenzofuran homologues by particle size. In summer, no clear peak was observed with TeCDDs/TeCDFs, pentachlorodibenzo-p-dioxins (PeCDDs)/pentachlorodibenzofurans (PeCDFs), and the gaseous component formed a very large proportion in these homologues. The high concentrations of TeCDDs/TeCDFs and PeCDDs/PeCDFs were observed in the smaller particle than in larger particles. With the hexa- to octa-chlorinated congener, dioxin concentration was relatively high even in the particles of less than 0.13 µm in diameter, and a peak was observed at around the particle diameter of 0.52 µm (fine particle diameter). In winter, TeCDDs/TeCDFs were detected in higher concentration in the gaseous phase compared with particles, and with all the homologues, a peak was observed around
Fig. 3. Comparison of Particle Diameter Distribution of PCDDs and PCDFs Congeners in Ambient Air between Summer and Winter, 2001

- □: summer, ■: winter.
0.52 \mu m particle size (fine particle diameter). Based on these results, we assume that the dioxins contained in coarse particles (larger than 1 \mu m), most of which are removed in the nasal passage, are less than 30% of the total in both seasons. We therefore believe that most of dioxins enter into bronchial tubes or lungs of the human body.

Concentration of Dioxins in Particles

From the fact that particle size distribution of dioxins varies depending on the homologue, a difference in dioxin compositions may be found among the particulate and gaseous phases in each class. Figure 4 illustrates the weight of dioxin and dibenzofuran homologues per unit particle weight (weight concentration) collected for each size-class. In both summer and winter, the smaller particle showed a tendency of higher weight concentration in dioxins except of TeCDDs/TeCDFs. However, regarding TeCDDs/TeCDFs, the highest weight concentration was seen in the particle of 0.13 \mu m, and the lowest was did in the particle of around 0.76 \mu m. In addition, another small peak was observed in coarse particles with a size of bigger than 1.25 \mu m.

Comparison of seasonal differences in particulate dioxin indicates that the pollution level was higher in winter than summer with TeCDDs/TeCDFs, PeCDDs/PeCDFs and HxCDDs. However, the reverse was observed in the levels of HpCDDs/HpCDFs and OCDF in smaller patticles. The level of HpCDDs/HpCDFs in larger particle was similar level in both summer and winter. Rordorf et al. reported vapor pressure of 2,3,7,8- TeCDD and OCDD were $4.7 \times 10^{-9}$ mmHg and $8.3 \times 10^{-13}$ mmHg, respectively.7) Because the difference of vapor pressure between dioxins is ca. $10^4$ mmHg, it is considered that most dioxin exists in suspended particles in winter, on the other hand, a part of low chlorinated dioxins were trapped as gaseous components. But, with OCDD in winter, the high weight concentration fraction was observed with the particles of 0.33 to 2.5 \mu m in diameter, and distribution pattern differed greatly from those of other homologues. Detailed survey is necessary to clarify such phenomena. Figure 5 indicates the composition ratios of dioxin and dibenzofuran homologues in particles, which allows the composition status to be assessed easily. Figure 5 also indicates the composition ratio

<table>
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<th>Table 1. Particle Diameter Distribution of PCDDs and PCDFs Congeners in Ambient Air, 2001</th>
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<tr>
<td>particle size(\mu m)</td>
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unit: pg/m$^3$ (pg-TEQ/m$^3$: TEQ)
of dioxin homologues in gaseous phase. As shown in this figure, the homologue composition varies depending on the particle diameter. The composition ratio of dioxin varied remarkable in particles with a size of 2.5 µm and bigger than 3.9 µm. The variations of TeCDDs/TeCDFs were very small in
Particle Diameter Distribution of Toxic Equivalent Quantity (TEQ) by Concentration of Suspended Particles in the Air

Various toxic equivalent factors (TEF) have been proposed depending on dioxin homologues, and toxic equivalent quantity (TEQ) can be calculated by multiplying each isomer concentration by TEF of the relevant isomer. The calculations of TEQ of dioxin and dibenzofuran in the air were shown in Table 1, and Fig. 6 illustrates the calculated particle size distribution of TEQ. In winter, a clear peak was observed around the particle diameter of 0.52 µm. In summer, however, a peak as clear as in winter was not observed.

Concerning the TEQ of in both summer and winter specimens, two-peak particle size distribution was not observed. More than 75% of TEQ was contained in gaseous phase and suspended smaller particles of 1 µm or smaller that 1 µm, that can easily reach inside the lung of the human body.

In conclusion, a great seasonal difference in the composition of dioxin congeners was recognized in gaseous phase and each size particle phase. The other hand, the difference of dioxin composition depend on particle size was not observed. It was suggested that dioxin was taken in the particle before fractionation of particles started. In addition, it was considered that low chlorinated dioxin with low molecular weight could preferentially accumulate to smaller size particles.

The above results indicate that in evaluating the effect of the deposition of toxic dioxins on the lung or their exposure to the respiratory tract, it is very important to take into consideration not only the weight and size air suspended particles or dioxin pollution level but also the composition of dioxins contained in those particles.

REFERENCES


