Assessment of Air pollution by Dioxin Analogues at Various Locations in Japan Using Japanese Black Pine Needle as a Biomonitoring Indicator

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Abstract
Air pollution by PCDFs, PCDDs and Co-PCBs various areas in Japan was evaluated by their accumulation levels in Japanese black pine needle as an indicator. In the survey of 19 areas in the whole of Japan, there was a remarkable regional difference in the atmospheric pollution with a level of 1.00 to 21.0 pgTEQ/g dry weight. On the other hand, similar observation was also recognized 20 locations in the Osaka area survey with the accumulation level of 2.14 to 31.4 pgTEQ/g dry weight, indicating the contamination level to be influenced on atmospheric stream and topography.

Introduction
The indeciduous Japanese black pine tree (*Pinus thunbergii parlatore*) grows in every areas except for Okinawa (the most southern prefecture) in Japan, and its needle has the lipophil cuticle on the surface. In 1996, we revealed that the pine needle accumulates effectively atmospheric pollutants of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofuran (PCDFs) and non-ortho chlorine substituted coplanar PCBs (Co-PCBs)[1]. In addition, their accumulation levels were rather stable after reaching plato levels, showing the variation to be within 2 times during a period of 3 months. Therefore, we tried to evaluate atmospheric pollution of dioxin analogues (PCDDs, PCDFs and Co-PCBs) using Japanese black pine needle samples from 13 areas in Japan[1].
In this study, another 6 areas in the whole of Japan were surveyed for air pollution by dioxin analogues. In addition, Osaka area, one of the highest air pollution regions by dioxin analogues, was minutely investigated using pine needle samples from 20 locations.

Experimental Methods

1) Sample

The whole country survey sample: About 1 kg of one year aged Japanese black pine needle sample was collected in Gifu, Ishikawa, Mie, Yamaguchi, Okayama and Hiroshima Prefectures, respectively, in March, 1995 to March, 1996. The sampling locations were respectively illustrated as the location Nos. of ⑧, ⑨, ⑩, ⑭, ⑮ and ⑯ in Fig. 1.

Osaka area survey sample: About 1 kg of one year aged black pine needle was respectively sampled at 20 locations shown in Fig. 2 during a period of December, 1995 to May, 1996. The details of sampling sites are described in Table 1.

Each needle sample was lyophilized, cut into a length of ca. 3 cm, and then stirred well up.

2) Analytical method

After spiking of internal standards (five $^{13}C_{12}$-PCDDs and five $^{13}C_{12}$-PCDFs, each 400 pg; three $^{13}C_{12}$-Co-PCBs, each 500 pg), 50 g of pine needle sample was homogenized with 250 ml of toluene by a ultramixture machine, and then extracted for 5 hrs. under reflux. After addition of silica gel (30 g), each extract was stirred and filtered for removing a bulk of chlorophyll. The filtrate was concentrated to less than 0.3 ml, followed by adjusting to a volume of 10 ml with n-hexane. The solution was cleaned up on a multi-layer column and alumina column according to our previous report[1]. The purified extract was dissolved in 20 μl of n-decane and analyzed for PCDFs, PCDDs and Co-PCBs in EI-SIM mode at a resolution of 8000 using a Hewlett Packard 5890J gas chromatograph-JEOL SX-102 mass spectrometer according our report described elsewhere[2].

Results and discussion

1) Whole country survey

Fig. 1 showed total TEQ concentrations of PCDFs, PCDDs and Co-PCBs in Japanese black pine needle from 19 areas in the whole of Japan. The TEQ was calculated on the basis of I-TEF[3] for PCDFs and PCDDs, and on the basis of WHO/IPCS-TEF for Co-PCBs. As shown in Fig. 1, the TEQ concentration was in a wide range of 1.00 to 21.0 pgTEQ/g dry weight. The TEQ range for each dioxin analogues were 0.29 to 16.4 pgTEQ/g for PCDFs, 0.02 to 4.58 pgTEQ/g for PCDDs and 0.01 to 4.33 pgTEQ/g for Co-PCBs. The contamination level was remarkably high at urban with commercial and/or industrial activity such as Yotsukaido in Chiba, Fujisawa in Kanagawa, Shimoda in Shizuoka, Nara in Nara and Sakai in Osaka. While the local areas with a small population density (114 to 608 persons/km^2) such as Date in Hokkaido, Kamaishi in Iwate, Ena in Gifu, Tokuyama in Yamaguchi and Tottori in Tottori showed the lower pollution level. However, the low pollution was recognized in Shibuya in Tokyo, Yokkaichi in Mie, Nougata in Fukuoka and Oita in Oita with a high population density (1,021 to 12,127 persons/km^2). Therefore, further investigation is necessary to resolve the air contamination degree.

Table 1 Details of sampling locations of black pine needle collected from Osaka, Kyoto and Nara prefectures

No.	Sampling date	Sampling place	Population (person)	Population density (person/km²)	Sampling point
Osaka Prefecture					
A-1	Mar. 13, '96	Osaka City	2,478,628	11,239	Industrial area
A-2	Mar. 9, '96	Osaka City			Urban area (1 m from National road)
A-3	Mar. 13, '96	Takatsuki City	360,009	3,419	1 m from highway
A-4	Mar. 13, '96	Takatsuki City			500 m from MSW incineration
A-5	Mar. 13, '96	Ibaraki City	251,899	3,292	Urban area
A-6	Mar. 15, '96	Neyagawa City	256,263	10,367	1 Km from MSW incineration
A-7	Mar. 15, '96	Neyagawa City			1.5 Km from MSW incineration
A-8	Mar. 15, '96	Neyagawa City			1 Km from MSW incineration (opposite of A-6, A-7)
A-9	Jan. 1, '96	Shijyonawate City	53,134	2,835	Residential area
A-10	Jan. 2, '96	Hirakata City	394,954	6,070	Residential area
A-11	Mar. 8, '96	Hirakata City			5 m from national road
A-12	Mar. 9, '96	Higashiosaka City	495,047	8,009	Residential area
A-13	Mar. 9, '96	Yao City	269,302	6,457	Residential area
A-14	Jan. 19, '96	Minamikawachi District			Residential area
A-15	Feb. 15, '96	Sakai City	794,379	5,808	Industrial area
A-16	Feb. 19, '96	Izumisano City	91,641	1,695	Residential area
Kyoto Prefecture					
B-1	Mar. 5, '96	Kyoto City	1,389,342	2,277	Urban area
Nara Prefecture					
C-1	Apr. 11, '96	Ikoma City	105,622	1,986	Residential area
C-2	May 21, '96	Nara City	356,471	1,685	Urban area
C-3	Dec. 22, '95	Nara City			Urban area

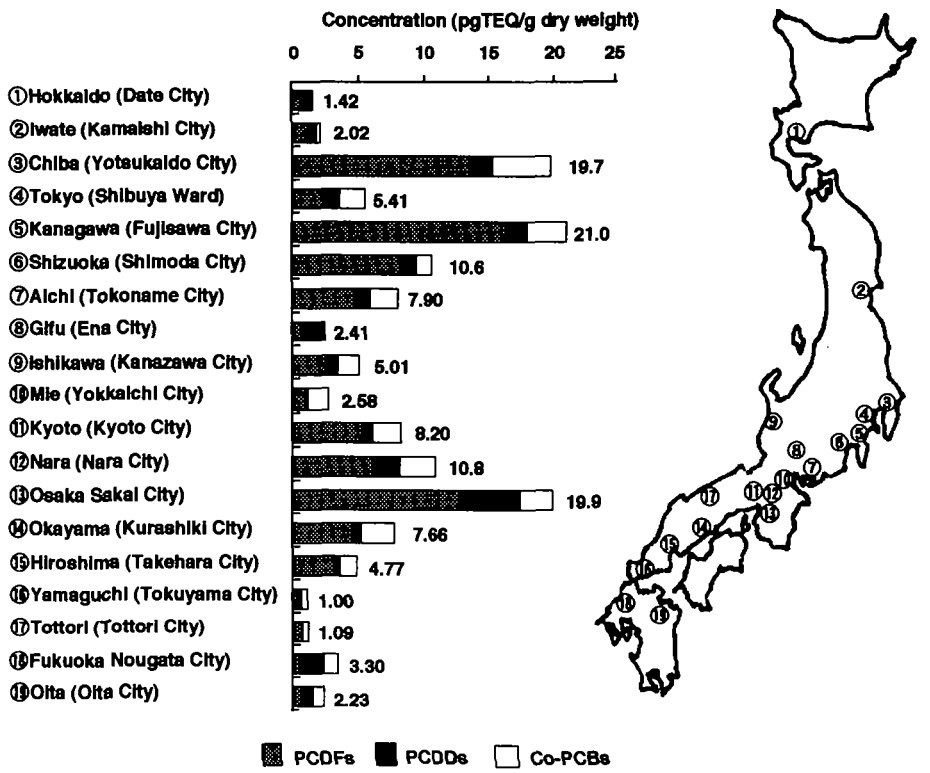

Fig. 1 Total TEQ concentrations (pg TEQ/g dry weight) of PCDFs, PCDDs and CoPCBs in black pine needle from various locations in Japan

2) Osaka area survey

As illustrated in Fig. 1, Wakamatsudai in Sakai, Osaka prefecture, was one of the highest air pollution areas in Japan. We also revealed that Osaka was the most heavy contamination area in a case of blue mussel monitoring for sea pollution[3] Therefore, in this study, we tried to investigate minutely atmospheric pollution by dioxin analogue in Osaka prefecture and its adjacent prefectures of Nara and Kyoto.

As well as in a case of whole country survey, there was observed a remarkable regional difference in the contamination level of dioxin analogues in Osaka area. As shown in Fig. 3, the total TEQ of PCDFs, PCDDs and Co-PCBs was in the wide range of 2.14 to 31.4 pgTEQ/g dry weight.

It is a noteworthy thing that the most heavy pollution was not observed at locations surrounding the municipal solid waste incineration facility such as sampling Nos. of A-4, A-6, A-7 and A-8, showing the level to be in the range of 3.63 to 20.9 pgTEQ/g. In addition, contrary to our expectations, Osaka City (A-1 and A-s) showed remarkably low pollution levels with 2.14 and 6.6 pgTEQ/g (Fig. 3), in spite of the highest population density (11,239 persons/km^2) among Osaka and its surrounding areas (Table 1), and its

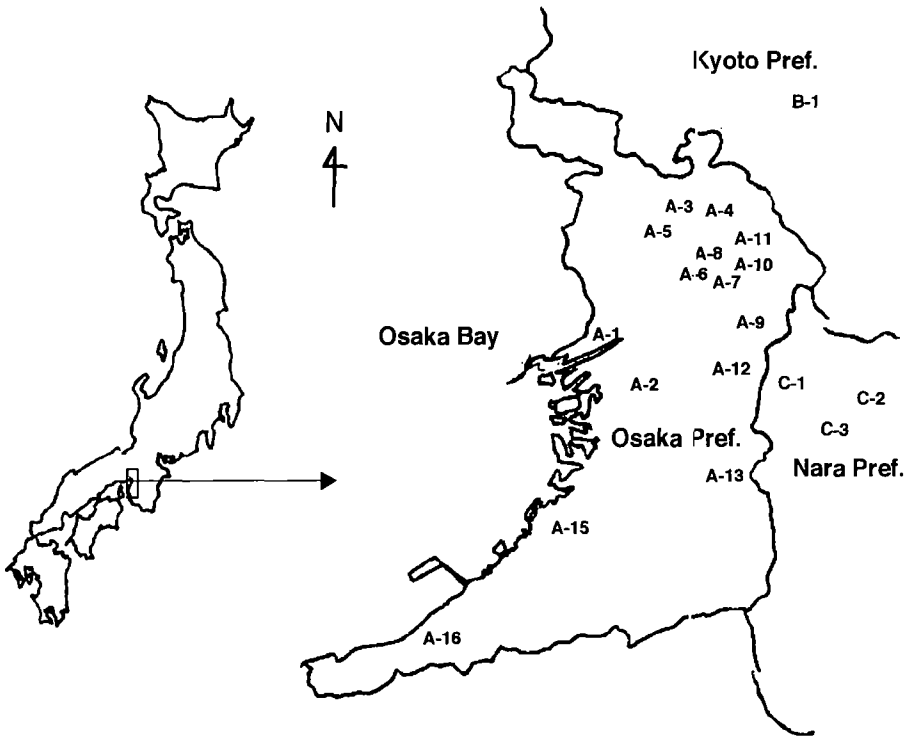

Fig. 2 Map of the sampling area of osaka, Kyoto and Nara prefectures

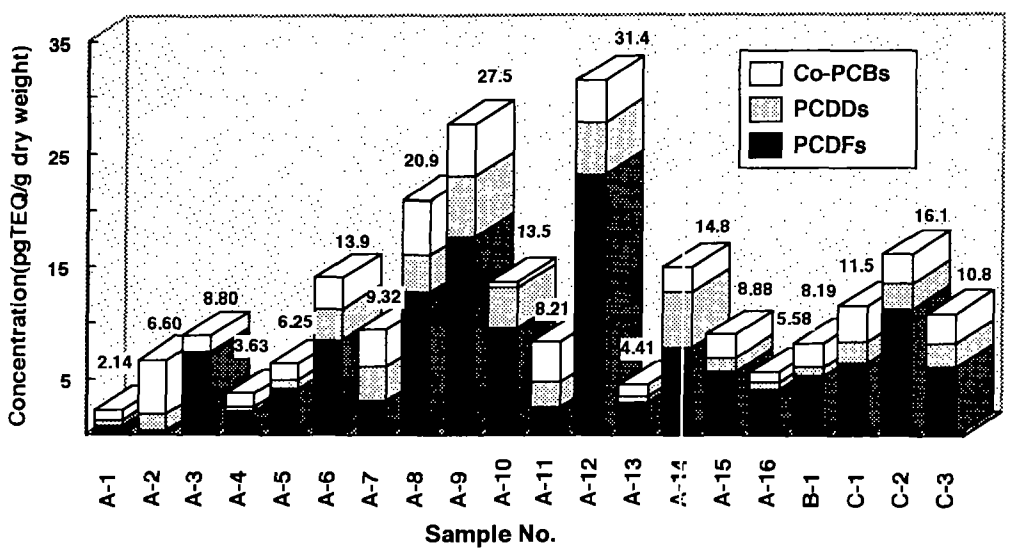

Fig. 3 Total TEQ concentrations of PCDFs, PCDDs andCo-PCBs, PCDFs in black pine needle samples collected from Osaka, Kyoto and Nara prefectures

highest commercial and industrial activities. As well as in a case of Osaka City, Sampling point A-15 (Hamadera town) in the central part of industrial area in Sakai City with a high population density (5,808 person/km^2) and a high industrial activity showed the low level of 8.88 pgTEQ/g. From these results, it is concluded that the low contamination in regions (A-1, A-2, A-15 and A-16) close to Osaka Bay might be attributable to spreading of atmospheric dioxin analogues to the Osaka Bay.

The Ikoma mountains is present in the borderline of Osaka and Nara prefectures. As shown in Fig. 3, the most heavy pollution was recognized at Higashiosaka City (A-12, 31.4 pgTEQ/g) close to the Ikoma mountains. In addition, the 2nd high level was observed at Sampling point of A-9 in Shijyonawate City with low industrial/commercial activities and a relatively lower population density of 2,835 person/km^2. It is well known that the air flows from central and southern Osaka prefecture to cities close to the Ikoma mounties, especially Higashiosaka City. Therefore, the heavy pollution in A-9 and A-12 might be brought from staying of atmospheric stream by the mountains. Ikoma and Nara Cities with poor industrial/ commercial activities and a relatively low population densities (Table 1) are bedroom towns for workers in Osaka prefecture. Their air pollution level (10.8 to 16.1 pgTEQ/g) was higher most cities of Osaka prefecture. These sampling place of Ikama and Nara are located in just opposite sites to the Ikoma mountains. From these result and situation, the heavy pollution is surmised to be mainly derived from atmospheric transportation of dioxin analogues emitted in cities, Osaka prefecture.

Acknowledgements

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