Real Situation of Environmental Pollution in Saitama Prefecture by Dioxin Analogues by Using Black Pine Needle

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Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and non-ortho chlorine substituted coplanar PCBs (Co-PCBs) have been recognized as persistent and ubiquitous organochlorine contaminants in environment. It is well known that these compounds show various toxicity such as carcinogenesis, teratogenicity and immunity toxicity etc. Therefore, much importance has been recently attached to the problem of environmental pollution by dioxin analogues, which released from about 20,000 incinerators, including MSW and industrial waste incinerator in Japan. Especially, environmental pollution by dioxin analogues has become a serious problem at the area of Kunugi mountain in Saitama prefecture, because of many MSW and industrial incinerators concentrates on such small area. Actually, high ratio (1.5-1.9 times) of the neonatal infant morality was observed in surrounding area of Kunugi mountain, for the last years, comparison with the average ratio of Saitama prefecture. Further, similar phenomenon was also observed in the east area of Saitama prefecture, which exist many incinerators. From the observation results, it is urgently needed that the real situation of air pollution by dioxin analogues in surrounding area of the incinerators in Saitama prefecture. By the way, it is extremely difficult to using the methods of high-volume sampler evaluate the air pollution by dioxins, because the daily level of dioxin analogues in the air is liable to variation even at the same sampling point. We develop new evaluation method for air pollution; we revealed that the indeciduous Japanese black pine tree (*Pinus thunbergii parlatore*) is one of the most suitable indicator for atmospheric pollution by dioxin analogues[1]. In addition, their accumulation level were rather stable after reaching plato levels, showing the variation to be within 2 times during a period of 3 months.

Therefore, we tried survey the air pollution by dioxin analogues using black pine needle

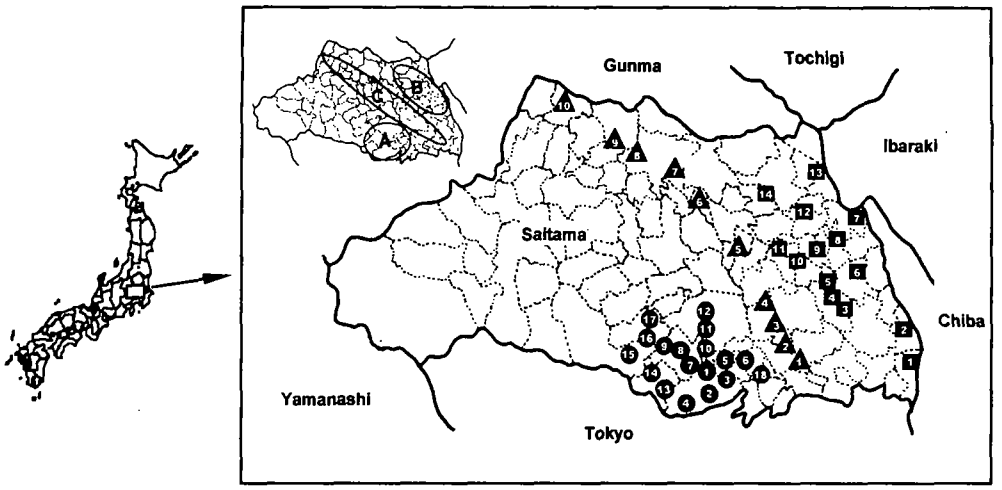

Figure 1 Map of the sampling points of Saitama prefecture in Japan

collected from surrounding area (A and B area) of the incinerators and high population density area (C area) in Saitama prefecture (as shown in Figure 1).

Experimental methods

1) Sample

As shown in Figure 1, Japanese black pine needle samples were collected from 42 points in Saitama prefecture during a period of June to September in 1997. Each needle sample was lyophilized, cut into a length of ca. 3 cm, and then stirred well up.

2) Analytical procedure

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 hr 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 containing Na_2SO_4 (2.0 g), 10%(w/w) $AgNO_3$-silica (8.0 g), silica (0.8 g), 22%(w/w) H_2SO_4-silica (4.0 g), 44%(w/w) H_2SO_4-silica (4.0 g), silica (0.8 g), and 2%(w/w) KOH-silica (3.0 g), silica (0.8 g) with an eluent of n-hexane (210 ml). The eluate was concentrated to and alumina column according to our previous report[1]. The purified extract was dissolved in 20 μl of n-decane and analyzed for PCDDs, PCDFs and Co-PCBs in EI-SIM mode at a resolution of 8000 using a Hewlett

Table 1 Evaluation of atmospheric pollution using black pine needle in Saitama prefecture

Sampling point*	Sampling location (city)	TEQ level (pg/g)	Judge.**	Sampling point*	Sampling location (city)	TEQ level (pg/g)	Judge.**
A-1	Shimotomi (Tokorazawa)	71.4	H	B-5	Heirinji (Iwatsuki)	19.9	M
A-2	Nakatomi (Tokorozawa)	28.7	H	B-6	Uchimaki (Kasukabe)	72.1	H
A-3	Sakanoshita (Tokorozawa)	43.2	H	B-7	Kidachi (Satte)	93.6	H
A-4	Kume (Tokorozawa)	40.0	H	B-8	Miyashirodai (Miyashiro)	21.6	M
A-5	Kamitome (Miyoshi)	36.1	H	B-9	Nekane (Hasuda)	94.6	H
A-6	Kitanagai (Miyoshi)	25.3	H	B-10	Hanuki (Ina)	45.7	H
A-7	Horikane (Sayama)	20.0	M	B-11	Gochoudai (Okegawa)	48.6	H
A-8	Mizuno (Sayama)	2.30	L	B-12	Washimiya (Washimiya)	39.8	H
A-9	Kashiwahara (Sayama)	12.3	M	B-13	Kitaookuwa (Ohtone)	54.6	H
A-10	Shimoakasaka (Kawagoe)	26.9	H	B-14	Kamitakayanagi (Kisai)	93.2	H
A-11	Imahuku (Kawagoe)	7.90	L	C-1	Minamiurawa (Urawa)	11.3	M
A-12	Wakitahonmachi (Kawagoe)	27.4	H	C-2	Honmachihigashi (Yono)	25.6	H
A-13	Miyadera (Iruma)	31.5	H	C-3	Horinouchicho (Ohmiya)	13.0	M
A-14	Araku (Iruma)	10.1	M	C-4	Yoshinocho (Ohmiya)	18.7	M
A-15	Hannou (Hannou)	9.60	L	C-5	Miyauchi (Kitamoto)	18.5	M
A-16	Kamikayama (Hidaka)	17.6	M	C-6	Kamatsuka (Fukiage)	49.2	H
A-17	Tabame (Hidaka)	14.5	M	C-7	Manpeicho (Kumagaya)	29.0	H
A-18	Kamiuchimaki (Asaka)	20.4	M	C-8	Nihori (Kumagaya)	43.7	H
B-1	Kakinokicho (Souka)	69.7	H	C-9	Nishijima (Fukaya)	10.0	M
B-2	Masumori (Koshigaya)	30.4	H	C-10	Ekinan (Honjyo)	15.9	M
B-3	Kakura A (Iwatsuki)	43.8	H	R-1	Date (Hokkaido)	1.40	L
B-4	Kakura B (Iwatsuki)	42.8	H	R-2	Hirakata (Osaka prefec.)	20.5	M

*Sampling point : See Figure 1, R : Reference point

**Judgement : H; High pollution area (> 25 pgTEQ/g), M; Middle pollution area (10-25 pgTEQ/g), L; Low pollution area (< 10pgTEQ/g)

Packard 5890J gas chromatograph-JEOL SX-102 mass spectrometer according our report described elsewhere[2]. Finally, to compare the toxic level by PCDDs, PCDFs and Co-PCBs in analyzed soil samples, the values of 2,3,7,8-TCDD toxic equivalent quantity (TEQ) were calculated for PCDDs and PCDFs using international 2,3,7,8-TCDD Toxicity Equivalence Factors (I-TEFs)[3] and for Co-PCBs using TEFs[4].

Results and discussion

As shown in Table 1, it was investigated that the total TEQ concentrations of PCDDs, PCDFs and Co-PCBs in Japanese black pine needle sample collected from 42 points in Saitama prefecture, and samples of Hirakata in Osaka prefecture and Date in Hokkaido as the reference points. Among 42 points analyzed, the TEQ concentration over 25 pgTEQ/g (High pollution area ; H) was observed in 25 points. In general, the level of dioxin analogues in pine needle was 10-20 pgTEQ/g in the population density area or industrial area of Japan[5]. Therefore, it

was beyond our conception that air pollution level in Saitama prefecture is progressing significantly.

Especially, in the A area, Shimotomi (A-1) in Tokorozawa was one of the highest air pollution areas, because a lot of industrial incinerators stand close together. The pollution level of A-1 were 3.5 times and 72.5 times, comparison with that of Hirakata (R-1 ; 20.5 pgTEQ/g) in Osaka prefecture as high pollution area, and that of Date in Hokkaido as low pollution area, respectively.

On the other hand, the atmosphere of almost city in B area were highly polluted, showing remarkable pollution level in Satte (B-7), Hashuda (B-9) and Kisai (B-14) (over 90 pgTEQ/g). The reason why indicate high air pollution in B area, was due to the existence of many incinerators, similar to the case of the A area. Further, it was also recognized that the samples collected from Fukiage (C-6) and Kumagaya (C-8) in the C area, were heavily pollution levels with 49.2 and 43.7 pgTEQ/g, respectively. Although we have already investigated the levels of dioxin analogues in about 300 black pine needle samples, which was collected from various areas in Japan, the levels in almost samples analyzed showed below 25 pgTEQ/g, whereas, in Saitama prefecture, 60% (25 areas) for analyzed samples (42 areas) were over 25 pgTEQ/g as high contamination area.

To elucidate the pollution sources in Saitama prefecture, it was try to compare the patterns of congener and isomer pattern. As a result, a lot of PCDF isomer was observed in almost samples, the isomer pattern was well accordance with combustion pattern. Further, the contribution of PCDF for total TEQ concentration showed over 50%. Therefore, air pollution by dioxins in Saitama prefecture was due to the flue gases and fly ashes from various incinerators.

Consequently, it has been concerned for bad influence of health condition of residents near by MSW incinerators.

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