Complex Pollution in Soil by Dioxin Analogues and Polycyclic Aromatic Hydrocarbons in Saitama Prefecture

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Introduction

Environmental pollution by dioxin analogues such as polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and non-ortho chlorine substituted coplanar PCBs (Co-PCBs) got to attract public attention in the world. As the reason, it is caused that dioxin analogues have extremely high toxicity, and expressed in various toxicities like carcinogenicity, reproductive toxicity, immunotoxicity and endocrine disruption.

Recently, much importance has been attached to the problem of environmental pollution by PCDDs, PCDFs and Co-PCBs released from municipal solid waste (MSW) incinerators in Japan, because the numbers of MSW incinerators and industrial waste incinerators were 1841 and over 20000 in our country, respectively. Especially, environmental pollution by dioxin analogues has become a serious social problem at the area of Kunugi mountain of Tokorozawa city (indicated No.1, 2 and 4) in Fig. 1) in Saitama prefecture, where industrial incinerators over 50 stand close together; the residents in its surrounding area are complaining of health damage like nausea and dizziness. In addition, from the result of epidemiological research, high ratio (1.5-1.9 times) of neonatal infant mortality was observed in surrounding area of Tokorozawa city, comparison with the average ratio of Saitama prefecture. Surprisingly, a similar phenomenon was also observed in many area of Saitama prefecture, where such incinerators stand close together.

In the last year, we evaluated for real situation of air pollution by dioxin analogues using the indeciduous Japanese black pine tree (*Pinus thunbergii parlatore*). As a results, among 42 points analyzed, the TEQ concentration over 25 pgTEQ/g was observed in 25 points[1)]. It was beyond our conception that air pollution level in Saitama prefecture is progressing significantly. On the other hand, it has been well known that polycyclic aromatic hydrocarbons (PAHs) having carcinogenesis are present as pollutants in environment. These compounds are formed during incomplete combustion of organic material, involving such processes as energy production, municipal incineration and in automobile engines utilizing internal combustion of fossil fuels[2)]. Therefore, in this article, we presents the levels of the environmental complex pollution by dioxin analogues and PAHs using soil, which collected from surrounding area (the area of A and B) of the incinerators and high population density area (C area) in Saitama prefecture (as shown in Figure 1).

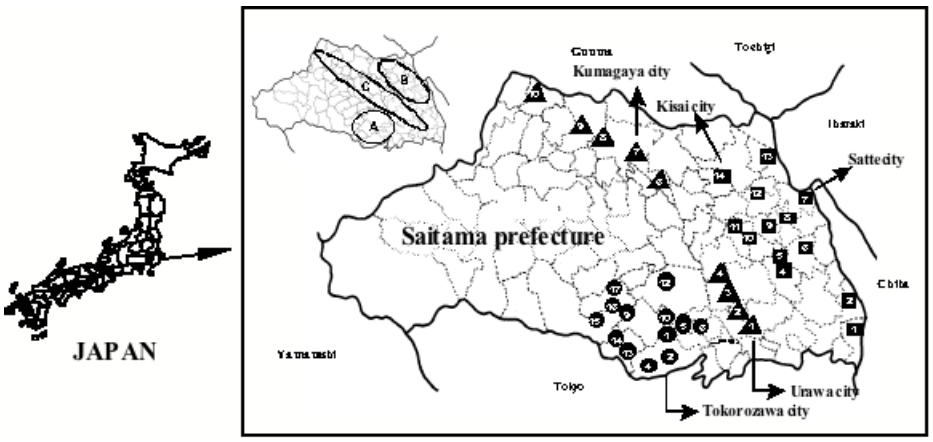

Fig. 1 Map of the sampling points of Saitama prefecture in Japan

Experimental methods

1) Sample : As shown in Figure 1, the surface soil samples (depth until 2-3 cm) were collected from 35 points in Saitama prefecture during a period of June to September in 1997. These samples were airdried and screened by 30 mesh strainer.

2) Analytical procedure : Ten g of soil sample on each sampling point was extracted with 250 ml of toluene for 5 hr under reflux. The toluene extract was passed through a 1 λm glass-fiber filter to remove soil particles. Then this filtrate was concentrated and replaced with 10 ml of n-hexane.

<Dioxin analogues> : The portion (5 ml) of extracts were spiked with a mixture of seventeen ^{13}C-labelled PCDDs/DFs and four ^{13}C-labelled Co-PCBs. Then, clean up of these extracts were performed on a multi-layer column chromatography and an alumina column chromatography. The purified extracts were used for analysis of gas chromatograph (GC)- mass spectrometer (MS) according our previous report described eleswhere[3].

<PAHs> : PAHs were analyzed according to EPA method TO-13 with minor modifications. The portion (0.1 ml) of extracts were spiked with a mixture of five deuterium labelled compounds (Naphthalene, Acenaphthene, Phenanthrene, Chrysene and Perylene). The solution was cleaned up on silica gel column (Merck, Kieselgel 60, 60-230 mesh, 10 g, activated on 3 hr at 130°C) with an eluent of 50% CH_2Cl_2/n-hexane (100 ml). The eluate containing PAHs was concentrated up to 3 ml, and then added 20 λl of n-decane as keeper solvent. The eluate was left for complete evaporation of n-hexane in room temperature and then adjusted to a volume of 20 λl with n-decane. Finally, 20 λl of eluate as purified sample was used for analysis of GC-MS. 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, PCDFs and Co-PCBs using WHO 2,3,7,8-

Table 1 Concentrations of dioxin analogues and PAHs in 35 soil samples of Saitama prefecture

Sampling point[*1]	Sampling location (city)	Dioxin analogues		PAHs[*3]	
		Act.[*2] (ng/g)	TEQ (pg/g)	Act.[*2] (ng/g)	B-TEQ (ng/g)
A-1	Shimotomi (Tokorozawa)	13.7	124	1980	110
A-2	Nakatomi (Tokorozawa)	12.5	136	1090	83.8
A-4	Kume (Tokorozawa)	1.41	14.4	691	3.40
A-5	Kamitomi (Miyoshi)	5.02	57.0	559	17.1
A-6	Kitanagai (Miyoshi)	8.78	91.9	1530	80.1
A-9	Kashiwara (Sayama)	12.9	424	N.A.[*4]	N.A.[*4]
A-10	Shimoakasaka (Kawagoe)	19.7	176	N.A.[*4]	N.A.[*4]
A-12	Wakitahonmachi (Kawagoe)	6.14	95.1	1420	118
A-13	Miyadera (Iruma)	15.4	236	N.A.[*4]	N.A.[*4]
A-14	Araku (Iruma)	3.98	46.9	713	13.8
A-15	Hannou (Hannou)	4.04	58.1	1410	27.1
A-16	Kamikayama (Hidaka)	10.7	211	1130	40.8
A-17	Tabame (Hidaka)	6.95	122	782	19.1
B-1	Kakinokicho (Souka)	12.1	119	1720	24.8
B-2	Masumori (Koshigaya)	15.8	94.6	638	22.3
B-4	Kakura B (Iwatsuki)	9.44	150	1100	71.5
B-5	Heirinji (Iwatsuki)	5.37	69.4	735	26.3
B-6	Uchimaki (Kasukabe)	5.28	35.9	1500	105
B-7	Kidachi (Satte)	27.0	291	574	11.1
B-8	Miyashirodai (Miyashiro)	15.4	62.3	N.A.[*4]	N.A.[*4]
B-9	Nekane (Hasuda)	15.7	164	1120	67.2
B-10	Hanuki (Ina)	27.8	121	951	50.4
B-11	Gochodai (Okegawa)	23.2	114	1230	50.6
B-12	Washimiya (Washimiya)	3.04	39.0	842	63.5
B-13	Kitaohkuwa (Ohtone)	18.0	157	1190	47.1
B-14	Kamitakayanagi (Kisai)	20.8	306	499	11.9
C-1	Minamiurawa (Urawa)	13.2	211	2610	246
C-2	Honmachihigashi (Yono)	4.06	61.2	N.A.[*4]	N.A.[*4]
C-3	Horinouchi (Ohmiya)	12.8	114	1740	117
C-4	Yoshino (Ohmiya)	1.42	39.7	N.A.[*4]	N.A.[*4]
C-6	Kamatsuka (Fukiage)	12.3	39.4	N.A.[*4]	N.A.[*4]
C-7	Manpei (Kumagaya)	9.71	103	1670	126
C-8	Niihori (Kumagaya)	3.07	33.0	936	33.9
C-9	Nishijima (Fukaya)	10.7	153	783	56.2
C-10	Ekinan (Honjyo)	2.97	27.7	N.A.[*4]	N.A.[*4]
R-1	Tanabe (Wakayama prefec.)	1.52	7.87	1070	86.3

*1 : Sampling point ; See Figure 1, R : Reference point
*2 : Act. ; Actual concentration (ng/g)
*3 : PAHs ; As follow 14 compounds (Naphthalene (Naph), 2-Methylnaphthalene (2-MeNaph), Acenaphthylene (Aceny), Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Phen), Anthracene (Ant), Fluoranthene (Fluor), Pyrene (Pyr), Benzo(a)anthracene (BaA), Chrysene (Chr), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP))
*4 : N.A. ; Not Analysis

TCDD Toxicity Equivalence Factors (WHO-TEFs)[4]. On the other hand, PAH toxic equivalent quantity were calculated as the amounts of Benzo(a)pyrene (B-TEQ) by using each PAHs-TEFs reported by Nisbet et al.[5]

Results and discussion

As shown in Figure 1, about six million people live in Saitama prefecture, which are located at 20 km in the north-west of Tokyo, Japan. Most large quantity of industrial wastes are treating in this prefecture of Japan. Therefore, it was also estimated that a large amount of dioxin analogues or PAHs were released from the incinerators. Table 1 shows the concentrations of dioxin analogues and PAHs in 35 soil samples collected from this prefecture. With respect to the TEQ concentration of dioxin analogues, high pollution over 100 pgTEQ/g was observed in 19 samples, and the rate was 54% in all samples surveyed. Especially, the incredible level of dioxin congeners was recognized in soils of Kashiwara (A-9), Miyadera (A-13), Kidachi (B-7) Kamitakayanagi (B-14) and Minamiurawa (C-1). It is generally known that the TEQ levels of dioxin analogues in soils of urban area were 15-30 pg/g, and that of rural or background area were below 10 pg/g in Japan[6]. Our observation results supported that the urgent measure against dioxin pollution involving industrial incinerator by administration is therefore needed.

On the other hand, the total actual concentration of PAHs was detected in the range from 499 to 2610 ng/g (Table 1). When the actual concentration was calculated as Benzo(a)pyrene toxin equivalent quantity (B-TEQ)[5], the levels of PAHs in Saitama prefecture were also extremely high. Interestingly, PAHs level did not always become high, comparison with the levels of dioxin analogues in the soils of same point. We considered that our observation is arised from the different emission sources like automobile etc. except the incinerators. High contamination by both substances was recognized in many soil samples, as seen in A-1, 2, 16, B-1, 9, 10, 11, 13 and C-1, 3, 4, 7, 9. It is well known that dioxin analogues like 2,3,7,8-TCDD indicated promotive activity for carcinogenesis, not mutagenesis, whereas PAHs like B(a)P indicated mutagenesity. Thus, it might be expected that simultaneous contamination for human by both substances occur various cancer at high rate. Consequently, it was assumed that the residents who live in the surrounding area of the above points have higher risk for carcinogenesis. Further study is planned to identify and determine the nitro-PAHs in soil samples of Saitama prefecture by GC-MS.

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