Formation of Dioxin Analogues by Open-air Incineration of Waste Wood and by Fire of Buildings and Houses Concerning to Hanshin Great Earthquake in Japan

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1. Introduction

In the early morning of 17th. January 1995, Hanshin Great Earthquake happened in the wide area of Hyogo and Osaka prefecture, which live in about 10 million people in Japan. The total number of death by the earthquake and the fire simultaneously caused was over 5000 people, and a lot of destroyed buildings and houses by them were generated in the area. A bulk of waste wood from the broken buildings and houses was consequently open-air incinerated during a period of February to May in five sites in Takaradzuka, Nishinomiya, Kobe and Amagasaki cities of Hyogo prefecture. After prohibition of open-air incineration by local government recommendation, 77,000 tons of wood scrap was also continued to burn in temporal incinerators in Nishinomiya and Amagasaki cities during a period of June, 1995 to October, 1996. It is well known that polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and coplanar PCBs (Co-PCBs) generate in the process of combustion of waste scraps. They are treated as so-called dioxin analogues due to their similar biological toxic effects. Further, Wunderli et al. (1996) reported that the burning of waste wood including paint, glue, plastics etc. formed considerably a high level of PCDDs and PCDFs, showing the 2,3,7,8-TCDD toxic equivalence quantity (TEQ) level in bottom ash samples to be 155 times on the average, as great as natural wood (5.3 pgTEQ/g)[1]. This suggests that a large amount of dioxin analogues might be released to environment by open-air incineration and fire concerning to Hanshin Great Earthquake. In this study, therefore, ash samples collected from sites of fire and the open-air incineration were analyzed for dioxin analogues in order to evaluate their formation by the combustion activities. In addition, Japanese black pine needle samples were also analyzed for assessment of atmospheric pollution by dioxin analogues concerning to wood scrap incineration in temporal incinerators.

2. Experimental materials

Ash samples were collected from open-air incineration sites in Kobe, Nishinomiya, Amagasaki and Takaradzuka cities, and from fire sites of houses and chemical shoe-making factories in Nagata ward, Kobe city in a period of one and two months after Hanshin great earthquake. Control soil samples were picked up at a distance of approximately 1 km from the open-air incineration sites in Nishi ward, Kobe city. All

samples were thinned in a thickness of 1 cm, left for 2 days at outdoor for complete dryness, and then pulverized into small particles. Each ash powdered sample was treated with 3% hydrochloric acid.
In addition, Japanese black pine needle samples were collected at the surroundings of temporal incinerators in order to assess atmospheric pollution of dioxin analogues by the incineration activity.

Analytical method
Ash and soil samples were respectively spiked with internal standards (five $^{13}C_{12}$-PCDDs and $^{13}C_{12}$-PCDFs, each 500 pg; three $^{13}C_{12}$-Co-PCBs, each 400 pg). The spiked ash sample (6.0 g) was extracted with 150 ml of toluene for 5 hrs under reflux, and the soil sample (20 g) was extracted with 500 ml toluene for 5 hrs under reflux. Just after the extraction, the hot toluene extract was filtered through filter with a 1 μm pore size in order to remove ash or soil particles. After addition of keeper solvent (n-decane, 0.3 ml), the filtrate was concentrated to a volume of less than 0.3 ml and adjusted to 20 ml with n-hexane. The adjusted filtrate was cleaned up on a multi-layer column containing Na_2SO_4 (8.0 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) with an eluent of n-hexane (210 ml). After concentrated to 10 ml, the eluate was separated into three fractions on alumina column chromatography (10 g, Merck neutral, activate I).
The third fraction was analyzed for PCDDs, PCDFs and Co-PCBs using a Hewlett-Packard gas chromatograph - JEOL SX102 mass spectrometer (R=7000-10000). The concentrations of PCDDs, PCDFs and Co-PCBs were corrected with the recovery of their respective internal standards. On the other hand, black pine needle sample was analyzed to according to our previous report[2].

3. Results and discussion

3-1) Ash sample survey

As shown in Table 1, all ash samples gave distinguishably higher total levels of PCDDs, PCDFs and Co-PCBs on the average with 28.9 ng/g dry weight in 16 open-air incineration sites, 28.3 ng/g in 13 house fire sites, 102 ng/g in 4 chemical shoe making factory fire sites and 2730 ng/g in electric appliances store fire site than did control soils (1.13 ng/g), showing the incineration and fire activities to form effectively three chemicals.
In a case of ash, Co-PCBs formed in almost same quantity in samples at four incineration/fire sites. However, the formation of PCDD and PCDF in ash of chemical shoe making factory and electric appliances store was remarkably larger than that of open-air incineration and house fire sites (Table 1). In particular, HpCDF and OCDF in ash of the electric appliances store were significantly high, showing their levels to be two to three digits greater than that of open-air incineration and house fire sites. The larger formation of PCDD and PCDF in ashes of chemical shoe making factory and electric appliances store sites might be attributable to the mixed combustion of chemical substances, such as plastic products and electric wires etc. In fact, it has been reported that combustion of plastic compose of polyvinyl chloride remarkably increase the amounts of PCDD and PCDF formation[3].
Figure 1 shows the total TEQ concentration of PCDDs, PCDFs and Co-PCBs, and their contribution to the total TEQ in ashes of the sites of open-air incineration and fire ashes.

Table 1 Concentrations (ng/g, dry weight) of PCDDs, PCDFs and Co-PCBs in various ash and control soil samples from Hanshin great earthquake

	Ash				Soil
	Wood scrap of broken building and house (n=16)	House (n=13)	Shoe-making factory (n=4)	Electric appliances store (n=1)	Control (n=3)
	Open-air incineration site	Fire site	Fire site	Fire site	
Compound	Concentration Mean (Max.~Min.)	Concentration Mean (Max.~Min.)	Concentration Mean (Max.~Min.)	Concentration	Concentration Mean (Max.~Min.)
2,3,7,8-TCDD	0.03 (0.14~0.00)	0.05 (0.23~0.00)	0.15 (0.21~0.04)	0.20	0.00 (0.00~0.00)
Total TCDDs	1.91 (14.0~0.01)	1.93 (9.26~0.38)	13.2 (20.9~3.58)	5.05	0.09 (0.24~0.01)
1,2,3,7,8-PeCDD	0.03 (0.23~N.D.)	0.04 (0.17~0.01)	0.23 (0.47~0.08)	1.19	0.00 (0.00~N.D.)
Total PeCDDs	0.91 (4.07~0.00)	1.09 (4.01~0.12)	10.4 (22.2~2.15)	5.07	0.01 (0.03~0.00)
2,3,7,8-HxCDDs	0.17 (0.62~0.00)	0.38 (1.87~0.02)	0.84 (1.87~0.22)	5.68	0.05 (0.15~0.00)
Total HxCDDs	1.87 (8.72~N.D.)	2.26 (5.41~0.12)	14.7 (25.3~1.81)	9.41	0.22 (0.63~0.00)
1,2,3,4,6,7,8-HpCDD	1.14 (6.04~0.05)	1.33 (5.48~0.01)	3.54 (7.63~0.32)	7.71	0.06 (0.17~0.01)
Total HpCDDs	2.36 (14.5~0.10)	3.08 (13.2~0.03)	7.48 (15.8~0.73)	8.69	0.09 (0.22~0.01)
OCDD	4.21 (39.6~0.25)	7.54 (50.7~0.10)	8.52 (17.4~0.59)	1.64	0.58 (1.10~0.31)
Total PCDDs	11.3 (62.8~0.43)	15.9 (69.9~0.76)	54.4 (101~8.85)	30.5	0.99 (2.22~0.36)
2,3,7,8-TCDF	0.46 (3.93~0.00)	0.09 (0.29~N.D.)	0.57 (1.02~0.24)	1.25	0.00 (0.00~N.D.)
Total TCDFs	5.84 (44.1~0.03)	2.72 (10.4~0.01)	15.0 (22.5~6.92)	3.40	0.02 (0.06~0.00)
2,3,7,8-PeCDFs	0.74 (6.48~0.00)	0.32 (1.12~N.D.)	2.15 (3.78~0.99)	2.52	0.00 (0.00~N.D.)
Total PeCDFs	3.99 (30.5~0.00)	2.24 (8.77~0.01)	11.7 (20.8~4.31)	5.80	0.02 (0.04~N.D.)
2,3,7,8-HxCDFs	1.08 (9.45~0.00)	0.96 (4.88~N.D.)	3.54 (7.16~1.47)	6.02	0.00 (0.00~N.D.)
Total HxCDFs	2.96 (18.7~N.D.)	2.09 (6.29~0.01)	8.72 (17.1~2.55)	7.81	0.03 (0.09~N.D.)
2,3,7,8-HpCDFs	1.32 (4.77~0.05)	1.77 (5.37~0.00)	4.55 (10.1~1.06)	1980	0.02 (0.06~N.D.)
Total HpCDFs	2.11 (11.5~0.05)	2.43 (7.89~0.01)	6.07 (13.3~1.50)	1980	0.02 (0.07~0.00)
OCDF	0.54 (3.01~0.01)	1.92 (9.55~0.01)	3.25 (6.27~0.71)	700	0.04 (0.11~0.00)
Total PCDFs	15.4 (106~0.59)	11.4 (31.0~0.05)	44.8 (80.0~16.0)	2700	0.13 (0.36~0.01)
3,3',4,4'-TCB	1.86 (10.7~0.00)	0.51 (2.26~0.11)	1.36 (1.97~0.50)	0.87	0.01 (0.01~0.00)
3,3',4,4',5-PeCB	0.29 (1.36~0.01)	0.33 (0.01~1.76)	0.91 (1.47~0.28)	0.74	0.00 (0.00~N.D.)
3,3',4,4',5,5'-PeCB	0.06 (0.25~0.00)	0.11 (0.65~0.01)	0.21 (0.45~0.05)	0.20	0.00 (0.65~0.01)
Total Co-PCBs	2.22 (10.7~0.12)	0.95 (4.68~0.24)	2.49 (3.89~0.83)	1.61	0.01 (0.01~0.00)
Total PCDDs+PCDFs	26.7 (143~1.02)	27.3 (90.3~5.33)	99.2 (181~24.8)	2730	1.12 (2.58~0.37)
Total PCDDs+PCDFs +Co-PCBs	28.9 (147~1.13)	28.3 (90.6~5.57)	102 (185~25.7)	2730	1.13 (2.58~0.38)

N.D. : Not Detected

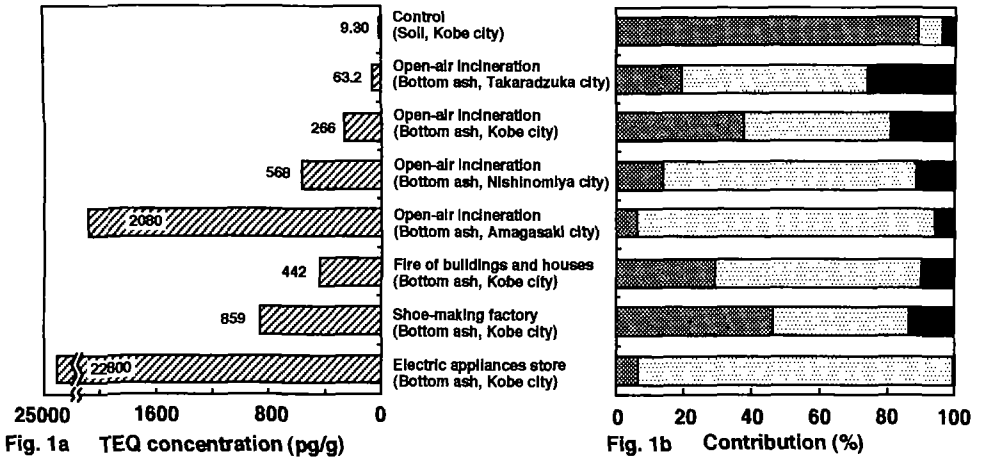

Figure 1 TEQ concentrations (Fig. 1a) and contributions (Fig. 1b) of PCDDs (▨), PCDFs (▭) and Co-PCBs (■) in ash samples from open-air incineration and fire sites

The TEQ concentration was a significant difference among four open-air incineration sites in Takaradzuka, Kobe, Nishinomiya and Amagasaki cities, showing the range to be 63.2 to 2080 pgTEQ/g. The ash of electric appliances store gave the highest TEQ level (22800 pgTEQ/g) among fire samples analyzed (Fig. 1a). Then, as shown in Fig. 1b, a ratio of PCDD to the total TEQ was remarkably lower in incineration and fire ashes (5~45%) than control soils (90%). The ratio had a decrease tendency with an increase of the total TEQ in ash samples. Contrary to this, the ratio of PCDF showed an increase tendency with an increase of the total TEQ. These results indicate that PCDF among dioxin analogues formed preferably in sites with a high TEQ such as Amagasaki and electric appliances. In a case of open-air incineration, there was a great difference in the TEQ level among four sites. This might be attributable to a discrepancy in the content of combusted wood scrap material in the four locations. A noticeable higher TEQ was observed in Amagasaki among incineration sites. The contribution pattern of dioxin analogues was similar to that of electric appliances store with the highest level of 22800 pgTEQ/g. Therefore, this suggests that the incinerated wood scrap might contain a greater content of metal and plastics than other incineration sites.

3-2) Evaluation of dioxin analogues formed by open-air incineration

As shown in Figure 2, PCDD and PCDF formed remarkably larger in open-air incineration activity of wood scrap than in forest fire of natural wood, showing the formation amount in ash to be 10 to 230 times greater in the former than the latter. The similar was also confirmed in a case of open-air incineration of waste and natural wood materials reported by Thomas et.al. (1994). Here again, we insist that incineration activity of recent wood materials containing of paint, plastics, etc. can produce substantially large amounts of dioxin analogues.

An amount of ash produced by this open-air incineration during a period of February to May, 1995 was totally 79,000 tons, shared by 9,000 tons in Takaradzuka, 20,000 tons in Amagasaki and 50,000 tons in Nishinomiya cities, respectively (Table 2). Therefore, a

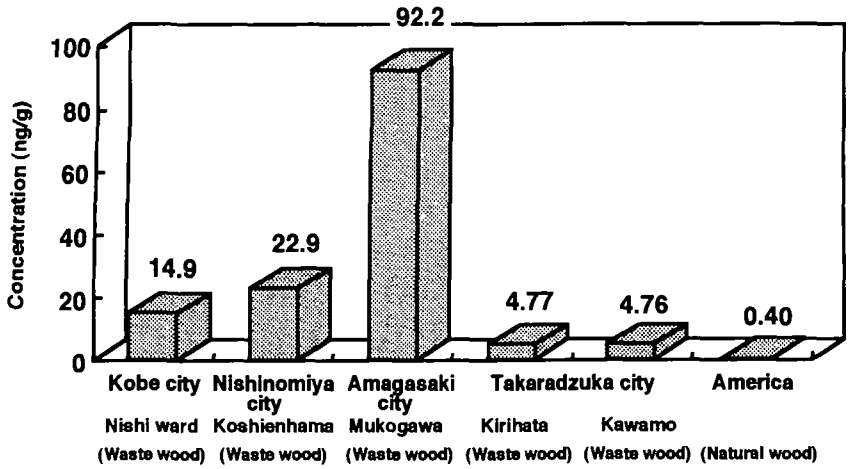

Fig. 2 Formations of PCDDs and PCDFs by open-air incineration of waste wood from Hanshin great earthquake

formation amount of dioxin analogues in the ash was calculated on the basis of our analytical data. Consequently, the formation amounts of PCDD, PCDF and Co-PCB in the three incineration sites was estimated to be 899, 2460 and 251 g, respectively, being equivalent to 6.56, 58.3 and 5.80 gTEQ, respectively. The total sum was 3160 g as actual amount and 70.7 g as TEQ amount. In a case of this open-air incineration, a substantially large amount of generated dioxin analogues is surmised to disperse into the atmosphere. In addition, the three incineration sites are located with 30 km with each other. Taking these things into consideration, it is concerned about adverse effects for many residents in the surrounding of incineration sites.

3-3) Black pine needle sample survey

After prohibition of open-air incineration, 77,000 tons of wood scrap was combusted during a period of June, 1995 to October, 1996 in temporal incinerators in Amagasaki and Nishinomiya cities. Therefore, we assessed atmospheric pollution by PCDDs, PCDFs and Co-PCBs at the surroundings of temporal incinerators using black pine

Table 2 Estimated amounts of PCDD, PCDF and Co-PCB formed by open-air incineration activity

Location of open-air incineration	Total amount of bottom ash (ton)	Estimation of dioxin analogue					
		PCDD		PCDF		Co-PCB	
		(g)	(gTEQ)	(g)	(gTEQ)	(g)	(gTEQ)
Nishinomiya city Koshienhama	50000	372	3.91	770	21.3	175	3.23
Amagasaki city Mukogawa	20000	507	2.54	1340	36.7	73.2	2.42
Takaradzuka city Kirihata, Kawamo	9000	20.1	0.111	350	0.311	3.01	0.147
Total	79000	899	6.56	2460	58.3	251	5.80

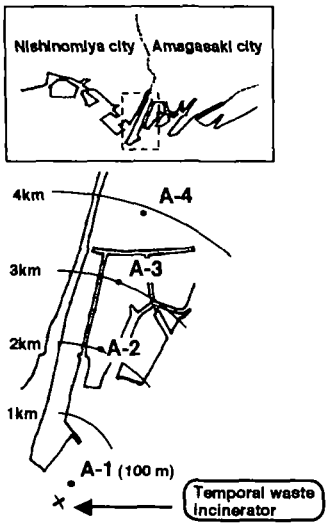

Fig. 3 Map of sampling points of black pine needle

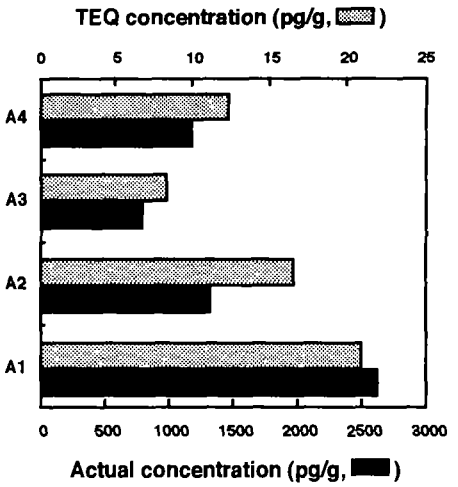

Fig. 4 Actual and TEQ concentrations of PCDDs, PCDFs and Co-PCBs in pine needle around the temporal incinerator in Amagasaki city

needle as an indicator. Figure 3 shows sampling points of pine needle at the surroundings of temporal incinerator in Amagasaki city, showing A1, A2, A3 and A4.

As illustrated in Figure 4, all pine needle samples on A line were heavily polluted with the levels of 794 to 2620 pg/g. Although TEQ level in pine needle sample of A1 as the nearest point was the most high (20.8 pg/g) on A line, it was also observed that the congener ratio of dioxin analogues in samples of A2-A4 was extremely similar to that of sample of A1. Therefore, after prohibition of open-air incineration, it was suggested that high atmospheric pollution by dioxin analogues at its surrounding area from the temporal incinerator was continued.

From all results, it could be clarified that the real situation of dioxin analogues pollution by the fire and the subsequent disposition of waste woods by the incinerator, arising from Hanshin Great Earthquake.

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