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Emission of Polychlorinated Dibenzo-*p*-dioxins and Polychlorinated Dibenzofurans from the Combustion of Municipal Solid Wastes Produced by a Natural Disaster

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Natural disasters such as earthquakes, floods and typhoons or hurricanes may produce large amount of municipal solid wastes (MSW). The management of such wastes becomes an enormous task for municipal authorities in the aftermath of disasters. Although many cities of the world have been devastated by such disasters every year, systematic studies on amounts of MSW produced by the disasters are rare. Studies on the management of disaster induced MSW are important for they can provide valuable information to people and authorities involved in disaster management. This study evaluates the aftereffect of one such natural disaster, the typhoon, on the generation of combustible solid wastes in a Japanese city. The Typhoon no. 18, passing through coastal areas of western Japan on 24 September 1999, caused widespread damage in the city. Resulting flood in coastal areas inflicted considerable damage to houses, agricultural products and forest resources. As a result, large amount of MSW was produced, which was subsequently combusted in the city incineration plant.

In this study, we estimated the amount of combustible solid wastes produced immediately after the disaster and analyzed polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in fly ash samples obtained from the municipal solid waste incineration plant, when the disaster induced additional wastes were combusted.

MATERIALS AND METHODS

The MSW incineration plant under investigation serves a population of about 175,000. It is a continuous type incinerator with a total capacity of 330 tons/day with three furnaces. The first and second furnaces each have a daily combustion capacity of 105 tons of wastes and that of the third furnace is 120 tons. Normally, the third furnace is operated daily accompanied either by the first or by the second furnace. The operating temperatures of all the three furnaces range from 800 to 900°C, and the temperature at the electrostatic precipitator (EP) inlet is approximately 280°C. The study was conducted after the occurrence of a devastating typhoon (Typhoon # 18), which passed across western prefectures

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of Japan on 24 September 1999. Storm surge brought huge mass of seawater to land areas, which flooded houses and damaged floor materials and furniture in coastal areas of the city where the incineration plant is located. Since 90% of the municipal solid wastes (MSW) is incinerated in the city, most of wastes produced and collected after the typhoon were brought to the incineration plant and combusted subsequently. Ten fly ash samples were obtained from EP outlet of the third furnace on different dates. One sample was collected before and nine samples were collected after the occurrence of the typhoon. The dates of collection and size of samples taken for further laboratory analysis are shown in Table 1.

Table 1. Fly ash sampling details.

Sample	Collection date	Sample wt. (g)	Dry weight (g)
I	23 April 1999	10	7.6
	24 September	**Typhoon no. 18**	
II	28 September 1999	10	8.0
III	29 September 1999	10	7.7
IV	30 September 1999	10	7.7
V	1 October 1999	10	8.0
VI	4 October 1999	10	8.2
VII	27 October 1999	10	8.4
VIII	29 October 1999	10	8.7
IX	2 November 1999	10	9.2
X	5 November 1999	10	8.7

Sample pretreatment and clean up were performed according to the official method of the Japan Ministry of Health and Welfare (Yasuhara et al. 2001). Briefly, the sample is pretreated with hydrochloric acid. After filtration, the liquid phase undergoes different steps of separation with water and dichloromethane. The solid phase is extracted with toluene using the accelerated solvent extractor (ASE 200, DIONEX). The instrumental conditions of extraction are given in Table 2.

Table 2. Instrumental conditions of extraction in accelerated solvent extractor.

Cycles	3
Heat	9 min.
Static	15 min.
Flush %	60 vol
Purge	120 sec.
Pressure	2000 psi
Temperature	180 °C
Solvent	Toluene 100%

As compared to Soxhlet, which takes almost 16 hours for extraction, ASE is very convenient, as the total time of extraction is not more than 2 hours. Richter et al. (1997) demonstrated that the extraction is equivalent to classical extraction methods. The volume of the extract is then reduced in a rotary evaporator to few mL dissolved in decane. After repeated addition of hexane and condensation, the sample is finally mixed up with hexane to obtain a volume of 5 mL for further cleaning up after spiking it with $[^{13}C_{12}]$-PCDD/Fs clean up spike. The clean up consists of two steps: combined silica and aluminium oxide columns. The sample concentrate, obtained after the silica gel column is further cleaned up with the alumina column chromatography and eluted with 75 mL 2% dichloromethane and 98% hexane portion (v/v). Subsequently, the PCDD/Fs fraction of the sample is eluted with 120 mL hexane/dichloromethane (1:1). After spiking the final extract with recovery standard solution, PCDD/Fs concentrations are determined using a GC system and a medium resolution mass spectrometry. Instrumental conditions of the GC/MS are shown in Table 3.

Table 3. Instrumental conditions of GC/MS

GC	Hewlett Packard HP6890	Injector temp.	260°C(SP-2331), 270°C(HP-5)
MS	JEOL GCmate MS-BU20		
Capillary columns		Ion chamber temp.	260°C
For T_4 to H_6	SP-2331: ϕ0.25mm × 60m, 0.20μm (film)	Ionization current	300μA
		Ionization voltage	37eV
For H_7 and O_8	HP-5: ϕ0.25mm × 30m, 0.25μm (film)	Ion accelerating voltage	2.5kV
Temp. program		Carrier Gas	He
SP-2331	150°C (2min) - (20°C/min) - 200°C - (2°C/min) - 260°C (35.5min)	Injection	Split/Splitless
		Ionization mode	EI
		Ion monitoring	SIM
HP-5	150°C (2min) - (20°C/min) - 200°C - (5°C/min) - 270°C (11.5min)	Resolution	3000

RESULTS AND DISCUSSION

The immediate aftereffect of the natural disaster can be judged from Fig. 1, which shows weekly variations in combustible solid wastes collection in the period of August to November of fiscal years 1998 and 1999. As evident from the figure, there was a marked collection of combustible solid waste in the immediate aftermath of the disaster. On average, the city collected around 1100 tons of combustibles per week in 1998. Before the typhoon, the weekly average was about 1200 tons in 1999. However, immediately after the typhoon on the fourth week of September, the amount increased to 2080, and on the first, second and third weeks of October the collections were 1435, 1340, and 1300 tons, respectively. Hence, as compared to weekly collection of previous fiscal year 1998, in 1999 an additional 1825 tons of combustible solid wastes were produced in the city immediately after the disaster. This amount is almost 45% of the average monthly collection of combustibles in the city. The municipality collected part of those wastes in the incineration plant pit with a total volume of 3500 m^3

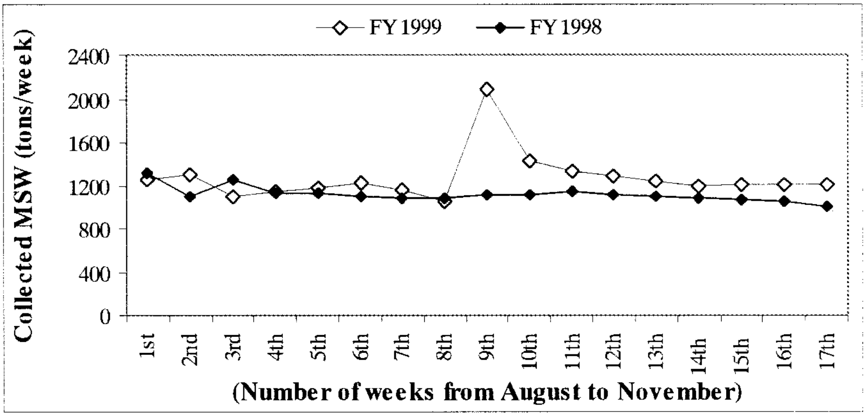

Figure 1. Weekly variation in combustible MSW collection from August to November (FY 1998 –1999).

and remaining wastes were stored in open spaces and gradually brought to the plant for combustion. It took almost six months to clear and incinerate all the additional wastes from the city. As a consequence, the activities of all three furnaces of the incineration plant increase markedly. As compared to a period of October to March of previous fiscal years, after the typhoon the number of hours of operation of the first and second furnace in 1999 increased by 37 and 71%, respectively and that of the third furnace increased by 5%. Due to the combustion of the additional wastes collected after the typhoon from October to March 1999, the incineration plant witnessed a 22% increase in generated ash compared to the production in the same period in 1998. Other effects of typhoon on various aspects of solid wastes management in the city are discussed elsewhere (Bhurtel et al. 2001).

Total concentrations of PCDD/Fs and corresponding toxicity equivalents (I-TEQ) of all ten fly ash samples obtained from the third furnace are illustrated in Fig. 2. An increasing pattern of total PCDD/Fs can be observed in samples obtained after the typhoon. On April 23, 1999, total yields of PCDDs and PCDFs were 2968 and 2127 ng/g, respectively. On October 27, however, the amounts increased to 4538 and 3242, respectively. Minimum total PCDDs as well as PCDFs with respective values of 1278 and 801 ng/g were found in sample obtained on November 5. As evident from the figure, all samples predominantly yielded PCDDs. On average, samples contained 60% of PCDDs and 40% of PCDFs with an average furan to dioxin ratio of 0.64. The TEQ yield was identical with the total concentrations. Maximum TEQ of 270 ng/g was detected in sample obtained on October 27. After the peak, the TEQ gradually dropped and the sample obtained on November 5 yielded the minimum TEQ of 49 ng/g. The average TEQ from all samples was found to be 125 ng/g. As a comparison, for example, in FY1997, the average concentration of PCDD/Fs in fly ash from the third furnace was only 73 ng/g. As shown in Fig. 2, the TEQ values of 16, and 180 ng/g detected in November 1997, and December 1999, respectively were provided by the incineration plant (IP).

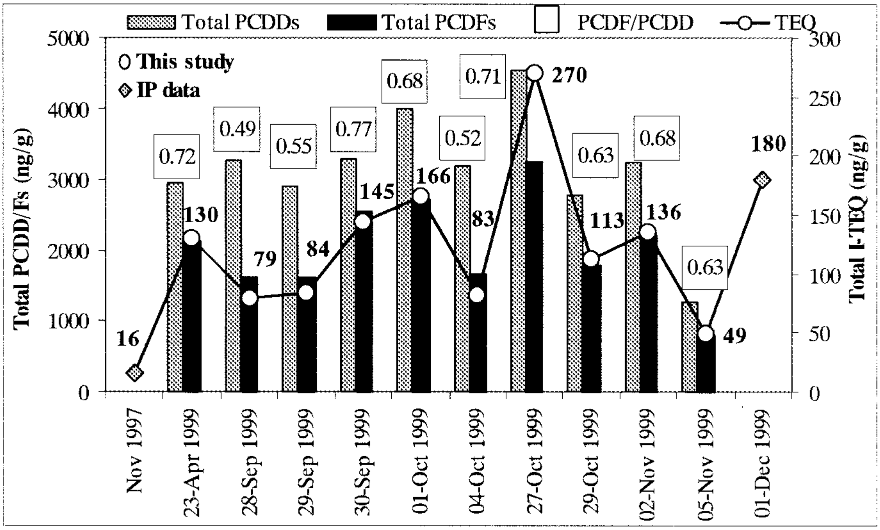

Figure 2. Total polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans and toxicity equivalents (TEQ) of fly ash samples.

As mentioned earlier, houses in coastal areas were flooded by the typhoon. Hence, most of the typhoon-induced wastes were soaked in seawater and contained high concentration of chloride. Especially on October 27 a large amount of seawater soaked floor materials, such as Japanese tatami mats, were incinerated in the plant. Higher PCDD/Fs emission on October 27 was possibly caused by the incineration of such wastes. The same reason might be true for overall rise in PCDD/Fs concentrations in samples obtained after the typhoon. There are several reports, which indicate that natural salt acts as an inorganic source of chlorine for the formation of PCDD/Fs at higher temperatures (Takasuga et al. 2000, Yasuhara et al. 2001). Since the melting point of NaCl is 800°C, combustion temperatures beyond the melting point cause higher vaporization of NaCl and formation of HCl and PCDD/Fs (Yasuhara et al. 2001). In large-scale incinerators, temperatures inside the furnace frequently reach the level enough to vaporize NaCl.

Concentrations of 17 toxic congeners and other homologues of all samples are depicted in Table 4. All isomers of PCDD/Fs were detected in all fly ash samples. Except the sample obtained on October 27, all other samples show similar homologue profiles of PCDD/Fs. In all samples, predominant congeners are PeCDD/Fs, HxCDD/Fs, and HpCDD/Fs. The furan to dioxin ratios were less than one for all samples and the maximum concentration of PCDDs was found in HpCDDs except in the sample of October 27, when the peak was observed at PeCDDs. Similarly, the minimum concentration was of the homologue with the highest degree of chlorination, i.e. OCDD. In general, the following homologues patterns were observed:

For PCDDs: T<O<Pe<Hx<Hp
For PCDFs: O<T<Pe<Hp<Hx

Table 4. Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans analysis of fly ash samples (ng/g).

PCDD/Fs	**23-Apr**	**28-Sep**	**29-Sep**	**30-Sep**	**1-Oct**	**4-Oct**	**27-Oct**	**29-Oct**	**2-Nov**	**5-Nov**
2378-TCDD	4.9	1.4	2.1	5.1	5.3	1.7	15.8	6.0	7.1	2.9
Other TCDDs	180.7	242.6	140.7	237.6	269.4	143.6	378.6	130.3	191.8	43.5
Total TCDDs	185.6	244.0	142.7	242.7	274.7	145.3	394.4	136.3	198.9	46.3
12378-PeCDD	74.4	31.4	43.3	89.5	99.9	35.2	228.1	75.2	77.2	22.8
Other PeCDDs	651.3	653.0	584.1	808.2	886.4	585.3	1356.3	663.2	637.1	254.8
Total PeCDDs	725.6	684.5	627.3	897.8	986.4	620.5	1584.3	738.4	714.3	277.7
123478-HxCDD	61.5	44.7	46.3	61.9	83.4	47.2	93.6	57.4	87.8	30.2
123678-HxCDD	89.3	75.1	57.1	75.8	115.9	70.5	133.1	64.6	99.0	38.5
123789-HxCDD	111.2	75.9	79.8	113.5	176.9	89.1	232.4	84.0	109.8	34.7
Other HxCDDs	576.4	749.3	528.0	564.4	772.9	637.1	692.2	530.7	775.0	349.1
Total HxCDDs	838.3	945.1	711.1	815.6	1149.1	843.9	1151.4	736.7	1071.6	452.5
1234678-HpCDD	339.1	358.8	368.0	372.7	455.9	419.1	441.9	329.0	332.6	137.0
Other HpCDDs	549.6	593.7	584.5	606.1	705.8	654.4	651.2	584.6	600.8	242.8
Total HpCDDs	888.7	952.5	952.4	978.7	1161. 7	1073.6	1093.2	913.6	933.4	379.8
OCDD	330.4	454.7	479.2	351.9	423.5	521.9	314.8	261.4	316.9	121.5
Total PCDDs	**2968**	**3281**	**2913**	**3287**	**3995**	**3205**	**4538**	**2786**	**3235**	**1278**
2378-TCDF	8.2	4.3	4.5	9.4	9.0	3.9	18.0	7.4	10.4	5.7
Other TCDFs	297.0	194.7	171.5	380.6	382.0	168.2	501.6	265.2	365.2	128.0
Total TCDFs	305.2	199.0	175.9	390.0	391.0	172.0	519.6	272.6	375.7	133.7
12378-PeCDF	34.7	19.9	19.8	43.5	45.5	19.1	92.6	35.7	38.3	17.3
23478-PeCDF	51.5	31.3	30.5	55.7	59.5	29.2	78.5	40.7	48.5	21.4
Other PeCDFs	488.8	332.1	325.1	580.0	626.2	318.2	804.0	447.1	515.0	210.6
Total PeCDFs	575.0	383.3	375.4	679.2	731.2	366.5	975.1	523.4	601.8	249.3
123478-HxCDF	86.1	49.9	44.5	89.0	89.5	44.5	129.1	54.3	76.4	27.6
123678-HxCDF	84.1	52.8	45.5	86.3	92.1	49.4	138.0	65.2	83.3	31.7
123789-HxCDF	4.9	4.1	5.6	8.6	8.7	6.5	13.0	3.6	3.9	2.0
234678-HxCDF	92.1	76.6	81.2	124.5	120.4	90.1	123.7	74.4	103.1	35.2
Other HxCDFs	477.6	339.0	319.7	567.4	606.2	332.4	739.4	386.1	510.1	177.2
Total HxCDFs	744.8	522.4	496.5	875.8	916.8	522.9	1143.2	583.6	776.7	273.8
1234678-HpCDF	258.8	204.4	248.4	300.9	313.8	252.4	334.2	209.5	250.6	78.7
1234789-HpCDF	38.0	43.2	47.4	55.0	66.2	59.4	60.6	28.0	29.9	10.2
Other HpCDFs	139.0	158.9	162.2	165.3	204.4	185.0	151.8	103.4	119.0	37.8
Total HpCDFs	435.9	406.5	457.9	521.1	584.4	496.8	546.6	341.0	399.5	126.7
OCDF	65.8	97.1	104.4	78.6	93.7	110.3	57.9	46.3	52.1	17.4
Total PCDFs	**2127**	**1608**	**1610**	**2545**	**2717**	**1668**	**3242**	**1767**	**2206**	**801**
Total PCDD/Fs	**5095**	**4889**	**4523**	**5831**	**6712**	**4874**	**7780**	**4553**	**5441**	**2079**

These results are in agreement with the observation made by Shin and Chang (1999) that after PCDD/Fs form on fly ash through various processes in MSW incinerators, small molecular weight PCDD/Fs congeners that have higher vapor pressure might be gasified and emitted through flue gas. Hence, congeners with a relatively higher molecular weight and lower vapor pressure remain more in fly ash. The only exception to this in these experiments were OCDD/F. In sample with highest TEQ value of October 27, PCDFs followed the above trend and PCDDs homologue distribution, however, showed the peak at PeCDDs.

The four-hour mean carbon monoxide concentrations in flue gas monitored online in the outlet of electrostatic precipitator did not show any abnormal variation on sampling days. On October 27, for example, the variation in CO concentration was 212±50 ppm, and on November 5, it was 222±88. Similarly, average O_2 content of flue gas was around 10% and the variations were insignificant. The quantity of combustible waste incinerated in the furnace also remained almost unchanged (100-118 tons per day) during the sampling period. Hence, it can be speculated that the variation in the composition of feeding waste on October 27 caused significant shifts in the formation of PCDD/Fs congeners. The TCDD and PeCDD/Fs with higher toxicity equivalency factor (I-TEF) increased drastically on that day causing a significant increase in the total TEQ value. From these observations as well as relative resemblance in congener patterns and furan/dioxin ratios in majority of samples, it can be assumed that the combustion conditions in the incineration plant remained approximately similar all through the sampling period. Hence, a considerable amount of PCDD/Fs emission from the incineration plant can be speculated due to the combustion of large amount of seawater soaked additional solid wastes produced by the disaster. However, due to the extraordinary situation, the composition of wastes and their chloride concentrations could not be investigated immediately after the occurrence of the disaster, which limited the possibility of understanding a more in-depth relation between the composition of wastes and PCDD/Fs emission.

This study also demonstrates the applicability of medium resolution GC/MC for the analysis of PCDD/Fs. Quantitative limit of PCDD/Fs determination (at S/N=10) in GC/MS is presented in Table 5, which shows the ability of the instrument to measure concentrations at very low levels.

Table 5. Minimum limit of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans determination.

PCDDs	Average quantitative limit (pg)	PCDFs	Average quantitative limit (pg)
TCDDs	3	TCDFs	2
PeCDDs	5	PeCDFs	4
HxCDDs	20	HxCDFs	20
HpCDDs	20	HpCDFs	4
OCDD	20	OCDF	10

It is generally accepted that the high-resolution gas chromatograph- high-resolution mass spectrometer (HRGC/HRMS) with a resolution of 10,000 is the preferred analytical instrument for PCDD/Fs analysis in environmental media. However, very high initial and maintenance costs involve with HRGC/HRMS prohibit its widespread use. Such prohibitive cost of analysis may limit frequency of PCDD/Fs measurements to inspect the compliance status of incineration plants and major objective of PCDD/Fs analysis will remain unfulfilled. Hence, scientific communities involved in dioxins research have been searching for alternatives to costly HRGC/HRMS. Recently GC/MS with a medium resolution of 3000 has been gaining popularity as an applicable alternative for the analysis of PCDD/Fs in media, such as fly ash, where high concentrations are found as demonstrated in this study. The use of high volume injector will widen its applicability and samples with low concentration of PCDD/Fs can be analyzed (JEOL). However, more experiments and analytical results are needed to make it a reliable instrument of PCDD/Fs analysis.

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