Dioxins in dust fall and volcanic ash samples from the active volcanos Fugendake and Sakurajima

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1. Introduction

There have been many reports on sources of chlorinated dioxins and related compounds[1]. Although the food ingestion is a very important route from the point of view of the human health risk by the dioxin(PCDD/F) exposure[2,3], the combustion and industrial processes such as waste incinerators, car exhausts and chemical and pulp industries, cigarette smoking, and hazardous waste disposal sites are also serious PCDD/F sources[4,5]. The interim international toxic equivalency factors(I-TEFs) recommended by NATO/CCMS as well as WHO/IPCS interim TEFs for human intake of dioxin-like PCBs recently reported[6,7], based on the available toxic data base, have been recognized, and set for PCDD/F risk chracterization in several countries, associated with the acceptable daily intakes (ADIs)[8].

We report here that volcanic activity also brings PCDDs/Fs, which have been found to form by combustion and/or to present as contaminants in agricultural chemicals etc., into the environment.

2. Materials and Methods

Dust fall from the volcano Fugendake was sampled with deposit gauges(vol. 20 L, 30 cm-I.D.) in Shimabara city in Nagasaki prefecture, and collected during from July 1 to 31 and September 29 to November 3 in 1992. Volcanic ash from the volcano Sakurajima was sampled from the campus of Kagoshima university in 1992. Analytical results of dust fall samples are shown in Table 1. Dust fall sample of about 600 ml and volcanic ash sample of 50 g were treated with acid (1 N-HCl), respectively. After filtering, the PCDDs/Fs in the residue was extracted by a Soxhlet extractor with 200 ml of toluene for 24 hrs, and the filtrate was shaken three times with 50 ml of toluene. These toluene solutions were mixed and concentrated. With 150 ml of n-hexane, the toluene condensate was treated

with sulfuric acid; the PCDDs/Fs in condensate were then separated by column chromatography with each 5 g of silica gel and activated alumina. The PCDDs/Fs in the eluate were extracted with toluene and concentrated up to 20 μ l. For high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) SIM analysis, 2 μ l of the toluene solution was used. Guaranteed-grade organic solvents from Wako Pure Chemical Co. Ltd.(Tokyo, Japan) were used in this study. Internal Standard materials, i.e., 1,2,3,4-TCDD($^{13}C_6$) and octa-CDD($^{13}C_{12}$) were supplied by Cambridge Isotope Laboratories(Woburn, MA) and each 10 ng was used for the determination of PCDDs/Fs. Conditions for HRGC/HRMS are provided in Table 2.

Table 1. Analytical results of dust fall samples(ton/km^2 per month)

Analyte/Date	Shimabara city 1992		Analyte/Date	Shimabara city 1992	
	Jul., 1-31	Sep.,29-Nov.,3		Jul., 1-31	Sep.,29-Nov.,3
Sample volume	12620 ml	4960 ml	pH	4.1(25℃)	4.6(19℃)
Total dust fall	374	178	SO_4^{2-}	0.6	0.4
soluble matter	3.4	2.4	NO_3^-	1.7	ND(0.00)
insoluble matter	377	176	Cl^-	ND(0.02)	0.5

Table 2. Conditions for HRGC/HRMS used to determine PCDDs/Fs

GC: HP 5890A-J, splitless type; MS: JMS-SX102
GC/column packing and temperature:
Supelco, sp-2331, 0.32 mm-I.D. x 60 m-L, thickness 0.17 μ m
100℃(1.5 min)→180℃→260℃(20 min), rate 1; 20℃/min, rate 2; 3℃/min
(internal STD, tetra- through hexa-CDDs/Fs)
HP-5, 0.32 mm-I.D. x 25 m-L, thickness 0.17 μ m
100℃(1.5 min)→180℃→290℃(1 min), rate 1; 20℃/min, rate 2; 10℃/min
(internal STD, hepta- and octa-CDDs/Fs)
GC/injection vol. and temp., and carrier gas: 2 μ l , 260℃ & 290℃, He
MS/ion source and temp.: EI mode, 1000 μ A(Δ m/e=10000), 250℃
MS/monitor ion: M^+, $(M+2)^+$ (isotope ratio; $\pm \leq 30\%$)

3. Results and Discussion

Tables 3 gives the PCDD/F concentrations and their TCDD toxic equivalents(TEQ) in dust fall and volcanic ash samples from the active volcanos Fugendake and Sakurajima. Hepta- and octa-CDDs/Fs were detected in dust and ash fall samples. Total PCDD/F concentrations were approximately 25 mg/km^2 or 0.1 mg TEQ/km^2 per month for dust fall samples, and were 5 pg/g or 0.03 pg TEQ/g for volcanic ash samples. For dust fall samples, tetra-, hexa- and hepta-CDDs other than 2,3,7,8-

substituted congeners were also identified in concentrations of a few mg/km^2 per month. PCDDs were higher concentrations in both samples than PCDFs. It has been reported that PCDD/F concentrations in ambient air range from a few to one hundred pg/m^3 and their equivalents vary between 0.02 - 2.3 pg TEQ/m^3 [9]. Rappe et al.[10] have noted that PCDDs/Fs in airborne particles are in the concentration ranges of 0.2 to 13.6 pg/m^3. In addition, in these atmospheric samples, traces of tetra- through octa-CDD/F congeners have been detected. However, the appearance patterns of these congeners were different from our results that only highly chlorinated substitutes of hepta- and octa-CDDs/Fs were present in dust fall and volcanic ash samples from the two volcanos. The dust fall and ash as well as airborne particulates, as a scavenger of atmospheric matter, are transported in the atmosphere. Although the samples used in this study were collected immediately after the volcanic eruption, further studies are necessary whether our results were mainly produced by volcanic activities or not attributed to the atmospheric matrix including PCDDs/Fs.

Table 3. Concentrations of 2,3,7,8-chlorine substituted PCDDs/Fs and their TCDD toxic equivalents in dust fall and volcanic ash samples from the active volcanos Fugendake and Sakurajima

PCDDs/Fs / Samples	Dust fall(Shimabara city)		Volcanic ash(Kagoshima city)	
	Jul., 1-31	Sep.,29-Nov.,3	No 1	No 2
Dioxins				
Tetra-CDD	ND(0)	ND(0)	ND(0)	ND(0)
Penta-CDD	ND(0)	ND(0)	ND(0)	ND(0)
Hexa-CDDs	ND(0)	ND(0)	ND(0)	ND(0)
Hepta-CDD	9.2(0.092)	5.2(0.052)	2.5(0.025)	1.8(0.018)
Octa-CDD	14(0.014)	11(0.011)	1.7(0.002)	2.2(0.002)
PCDDs	23(0.11)	16(0.063)	4.2(0.027)	4.0(0.020)
Dibenzofurans				
Tetra-CDF	ND(0)	ND(0)	ND(0)	ND(0)
Penta-CDFs	ND(0)	ND(0)	ND(0)	ND(0)
Hexa-CDFs	ND(0)	ND(0)	ND(0)	ND(0)
Hepta-CDFs				
1,2,3,4,6,7,8-	1.9(0.019)	2.8(0.028)	1.2(0.012)	1.2(0.012)
1,2,3,4,7,8,9-	ND(0)	ND(0)	ND(0)	ND(0)
Octa-CDF	4.2(0.004)	1.8(0.002)	ND(0)	ND(0)
PCDFs	6.1(0.023)	4.6(0.030)	1.2(0.012)	1.2(0.012)
PCDDs/Fs	29(0.13)	21(0.093)	5.4(0.039)	5.2(0.032)

Note. Values in the parenthesis are 2,3,7,8-TCDD toxic equivalents using I-TEFs.
Dust fall; mg/km^2 per month, Ash; pg/g, ND; not detected(0.5 mg/km^2 per month and 0.1 pg/g for tetra- through hexa-CDDs/Fs, 1.0 mg/km^2 per month and 0.5 pg/g for hepta- and octa-CDDs/Fs)

4. References

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