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REAL SITUATION ON EMISSION OF PCDDS, PCDFS AND NON-ORTHO CHLORINE SUBSTITUTED COPLANAR PCBS VIA FLUE GAS FROM URBAN WASTE INCINERATORS IN JAPAN

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INTRODUCTION

Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and non-ortho chlorine substituted coplanar PCBs (Co-PCBs) exhibit similar physical, chemical and biological properties with each others. Therefore, these three classes of chemicals are treated as so-called Dioxin analogues or Dioxin related compounds[1]. In recent years, they have been the subject of much concern in the environmental field in various countries, because some of PCDDs, PCDFs and Co-PCB isomers are extremely toxic.

Since Olie et al. (1977)[2] found PCDDs and PCDFs in samples from municipal waste incinerators in The Netherlands, extensive studies on these compounds have been made in various countries. Up to date, however, there are few reports on generations of Dioxin related compounds including Co-PCBs at municipal wastes incinerations in our country.

In this study, flue gas samples from urban waste incinerators were collected and analysed for PCDDs, PCDFs and Co-PCBs, and their daily emitted amounts via flue gas from waste combustion facilities were estimated.

EXPERIMENTAL

Sampling

Samples of flue gas were collected from ten waste incinerators with large combustion capacity of 90 to 600 tons/day (average: 320 tons/day) at big urban cities and the suburbs in 1992. The sampling volume was in the range of 2.8 to 3.3 Nm^3. The sampling method was as follows.

Probe: water cooled glass probe
Dust collection: cylindrical thimble glass-fiber filter
Inpingers: cooled water (150 ml)(before Amberlite XAD-2 resin), cooled water (300 ml)(before Amberlite XAD-2 resin) and cooled diethylene glycol (after XAD-2)
Adsorbent: Amberlite XAD-2 resin

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Extraction

Solid samples (cylindrical thimble glass fiber filter and XAD-2 resin) were Soxhlet extracted with toluene for 16 hours. Liquid samples (drain, washing methanol for inlet line and diethylene glycol) were extracted with toluene by mechanical shaking.

Clean-up

All toluene extracts were combined and concentrated to a volume of 100 ml. After addition of keeper solvent (n-decane, 1 ml), an aliquot of extract was concentrated to a volume of less than 1 ml and adjusted to a volume of 20 ml with n-hexane. After spiking internal standards (five $^{13}C_{12}$-PCDDs, five $^{13}C_{12}$-PCDFs and three $^{13}C_{12}$-Co-PCBs), the extract was purified on a multi-layer column containing Na_2SO_4 (2.0 g), 10% (w/w) $AgNO_3$-silica (2.0 g), silica (0.6 g), 22% (w/w) H_2SO_4-silica (4.0 g), 44% (w/w) H_2SO_4-silica (3.0 g), silica (0.6 g) and 2% (w/w) KOH-silica (2.0 g) with an eluent of n-hexane (80 ml). The eluate was concentrated to 3 ml and chromatographed into two fractions with successive eluents of 90 ml of 1% methylene chloride in n-hexane and 200 ml of 50% methylene chloride in n-hexane on an alumina column (10 g, Merck neutral, activate I). The second eluate containing PCDDs, PCDFs and Co-PCBs was concentrated to 3 ml. After addition of keeper solvent (n-decane, 30 ul), the concentrated eluate was left for complete evaporation of n-hexane at a room temperature and then adjusted to a volume of 100 ul with n-decane.

Above finally purified extract was analyzed on J & W DB-5 (30 m x 0.32 mm, 0.25 um)(held for 1 min at 140° C, programmed to 220° C at 20° C/min and to 310° C at 8° C/min, and held for 4 min) for hepta- and octachlorinated PCDDs and PCDFs, on Chrompack CP-Sil 88 (50 m x 0.32 mm, 0.20 um) (programmed for 150 to 180° C at 30° C/min and to 230° C at 2° C/min, and held for 29 min) for tetra- through hexachlorinated PCDDs and PCDFs, and on J & W DB-5 capillary columns(30 m x 0.32 mm, 0.25 um)(held for 1 min at 120° C, programmed to 180° C at 20° C/min, to 290° C at 8° C/min and 310° C at 20° C/min, and held for 2 min) for Co-PCBs in an elecron impact-single ion monitoring mode at a resolution of 7000 using a Hewlett Packard 5890J gas chromatograph-JEOL SX-102 mass spectrometer. The results were corrected for the recovery of $^{13}C_{12}$-labeled internal standards.

RESULTS AND DISCUSSION

All waste incinerators where flue gas samples were collected have a large combustion capacity of 90 to 600 tons/day (average: 320 tons/day). These facilities daily exhausted 2,230,000 m^3 of flue gas on average.

Table 1 to 3 show the average and range of daily emitted amounts of PCDDs, PCDFs and Co-PCBs via flue gas per incineration plant. In the case of PCDDs, the amounts of toxic 2,3,7,8-chlorine substituted PCDDs (2,3,7,8-PCDDs) roughly increased with increasing number of chlorine in the molecule. The average was 1.65 mg in 2,3,7,8-TCDD, 8.88 mg in 1,2,3,7,8-PeCDD, 9.65 mg in 1,2,3,7,8-HxCDD, 18.2 mg in 1,2,3,6,7,8-HxCDD, 12.4 mg in 1,2,3,7,8,9-HxCDD, 28.4 mg in 1,2,3,4,6,7,8-HpCDD and 22.7 mg in OCDD (Table 1). As shown in Table 2, the emitted pattern of 2,3,7,8-PCDFs was different from that of 2,3,7,8-PCDDs, that is, the levels of 2,3,7,8-PCDF isomers except 1,2,3,7,8,9-HxCDF and 1,2,3,4,6,7,8-HpCDF were roughly similar with each others, in spite of a difference in their chlorination degree. In general, there was observed a tendency that PCDF congeners had

larger emitted amounts than did PCDD ones, when substituted with same number of chlorine. For example, 2,3,7,8-TCDF (26.2 mg) and 1,2,3,7,8-PeCDF (40.9 mg) ewspectively showed 16 and 4.6 times higher amounts of 2,3,7,8-TCDD (1.65 mg) and 1,2,3,7,8-PeCDD (8.88 mg).

Incidently, the average daily exhausted amounts of Co-PCBs were 15.5 mg in 3,3'4,4'-TCB, 25.2 mg in 3,3'4,4',5-PeCB and 11.5 mg in 3,3'4,4',5,5'-HxCB. It is a noteworthy thing that the most toxic 3,3'4,4',5-PeCB among Co-PCB isomers showed the highest level.

The International 2,3,7,8-TCDD Toxicity Equivalency Factor (I-TEF) method[3] and 2,3,7,8-TCDD Toxicity Equivalency Factor (TEF) method by Safe et al.[4] respectively are updated interiums for estimating the risks associate with complex mixtures of PCDDs/PCDFs and Co-PCBs. These approaches facilitate the risk communication internationally by reducing large volumes of analytical data into a single number of the 2,3,7,8-TCDD Toxicity Equivalency Quantity (TEQ) for Dioxin analogues. Therefore, the TEQ for PCDDs/PCDFs and Co-PCBs in our flue gas samples were calculated by using above the I-TEF and TEF methods. As shown in Table 1 to 3, the average TEQ for PCDDs, PCDFs and Co-PCBs were 11.0, 40.3 and 3.25 mg. This indicates the magnitude of environmental impact is PCDFs>PCDDs>Co-PCBs. Thus tendency which Co-PCBs gave smaller TEQ value than did PCDDs or PCDFs was observed in all tested incineration facilities, indicating the ratios of Co-PCBs versus PCDDs and Co-PCBs versus PCDFs to be 0.004 to 0.472 (averagae: 0.173) and 0.008 to 0.106 (average: 0.057), respectively.

Now, we are trying to survey flue gas sample from another 15 urban wastes incinerators.

CONCLUSION

Flue gas samples were collected from 10 wastes incinerators with a big combustion capacity in big urban cities and the suburbs in Japan, in order to evaluate a real situation for Dioxin analogues emitted into the air through the flue gas. Consequenlty, average daily amounts (mg/incineration factory) of 2,3,7,8-PCDDs, 2,3,7,8-PCDFs and Co-PCBs were 188, 455 and 52.2 mg. In addition, their TEQ levels (mg/incineration factory) were 11.0, 40.3 and 3.25 TEQ mg, respectively. This indicates PCDFs give higher environmental impact than do PCDDs or Co-PCBs.

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Table 1. Average daily emitted amount of PCDDs per urban waste incineration plant

Compound	Daily emitted amount (ng) Average	(Minimum~Maximum)
2,3,7,8-TCDD	1.39	(0.022~6.43)
Others	201	(0.491~719)
1,2,3,7,8-PeCDD	8.88	(0.020~31.7)
Others	210	(0.390~680)
1,2,3,4,7,8-HxCDD	9.65	(0.032~41.7)
1,2,3,6,7,8-HxCDD	18.2	(0.031~93.8)
1,2,3,7,8,9-HxCDD	12.4	(0.029~59.8)
Others	246	(0.863~1170)
1,2,3,4,6,7,8-HpCDD	75.2	(0.440~184)
Other	78.6	(0.580~222)
OCDD	61.5	(0.490~163)
Total TEQ	11.0	(0.044~31.5)

Table 2. Average daily emitted amount of PCDFs per urban waste incineration plant

Compound	Daily emitted amount (ng) Average	(Minimum~Maximum)
2,3,7,8-TCDF	26.2	(0.099~114)
Others	1010	(1.83~4360)
1,2,3,7,8-PeCDF	40.9	(0.10~180)
2,3,4,7,8-PeCDF	34.9	(0.083~137)
Others	557	(1.24~2610)
1,2,3,4,7,8-HxCDF	49.0	(0.14~183)
1,2,3,6,7,8-HxCDF	46.4	(0.24~170)
1,2,3,7,8,9-HxCDF	6.05	(0.04~21.4)
2,3,4,6,7,8-HxCDF	67.5	(0.12~239)
Others	333	(0.99~1390)
1,2,3,4,6,7,8-HpCDF	109	(n.d ~304)
1,2,3,4,7,8,9-HpCDF	19.7	(n.d ~66.6)
Others	64.7	(n.d ~173)
OCDF	55.2	(0.09~231)
Total TEQ	40.3	(0.13~150)

n.d.: Not detected

Table 3. Average daily emitted amount of Co-PCBs per urban waste incineration plant

Compound	Daily emitted amount (ng) Average	(Minimum~Maximum)
3,3',4,4'-TCB	15.5	(0.04~71.7)
3,3',4,4',5-PeCB	25.2	(0.018~119)
3,3',4,4',5,5'-HxCB	11.5	(n.d.~65.6)
Total TEQ	3.25	(0.010~15.7)

n.d.: Not detected