CONTAMINATION OF DIOXINS AND RELATED COMPOUNDS IN SOILS COLLECTED FROM DUMPING SITES OF MUNICIPAL WASTES IN ASIAN DEVELOPING COUNTRIES

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Introduction

Dioxins and related compounds such as polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), and coplanar polychlorinated biphenyls (coplanar PCBs) are lipophilic contaminants and ubiquitous in the environment. A large number of monitoring studies have been conducted in developed countries during the last few decades. It has been suggested that residue levels of dioxins and related compounds in various environmental media and biota have generally decreased (1), because of complete adjustment of highly efficient incinerators and strict regulation for the production, usage and transportation of various chemicals.

On the other hand, in dumping sites of municipal wastes in Asian developing countries, a lot of various wastes have been dumped daily and continuously burned under low temperature by spontaneous combustion or intentional incineration. This is anticipated that dioxins and related compounds have been secondarily formed by combustion of wastes and surrounding environment has been polluted by these contaminants. To our knowledge, however, no study has reported the status of contamination for dioxins and related compounds in the dumping sites of Asian developing countries.

The present study attempted to elucidate the contamination of dioxins and related compounds in soils collected from dumping sites of municipal wastes and surrounding areas in Cambodia , India, Vietnam, and Philippines.

Materials and Methods

Soil samples were collected from the dumping sites of municipal wastes in Meanchey, Phnom Penh in Cambodia on Mar. and Nov. 1999 and Dec. 2000, Perungudi, Chennnai in India on Aug. 2000, Tay Mo, Hanoi in Vietnam on Apr. 2000 and Payatas, Quezon in Philippines on Aug. 1999, which are located in the suburbs of urban area. In addition, samples were also collected from surrounding areas of dumping sites in India, Cambodia and Vietnam. Soil samples were dried under the room temperature for four weeks, sieved through a 2-mm mesh screen for dioxins and related compounds and 0.5-mm mesh screen for copper, and stored at –20 °C until analysis.

LEVELS IN ABIOTIC COMPARTMENTS

Soil samples were extracted with toluene for more than 16 hours using a Soxhlet apparatus, and spiked internal standards ([^{13}C]-PCDDs, PCDFs, and coplanar PCBs). The extract was concentrated and dissolved in hexane. The hexane-dissolved extract was treated with concentrated sulfuric acid until the sulfuric acid layer became clear, and washed with hexane-washed water. Then the extract was passed through multilayer silica-gel packed in a glass column. Separation of PCDD/PCDFs and coplanar PCBs fraction was performed by passing through carbon-dispersed silicagel packed in a glass column. Identification and quantification of PCDDs, PCDFs, non- and mono-*ortho* coplanar PCBs were performed using HRGC (Agilent 6890)-HRMS (JEOL JMS-700D and GCmate).

TEQs (toxic equivalencies) were calculated using human/mammal-TEFs of WHO (2).

For analysis of copper in soils, the soil samples were treated with the HF-NHO_3-$HClO_4$ and digested by heating at 150 °C. Quantification of copper was performed by ICP-MS (HP-4500).

Results and Discussion

Dioxins and related compounds were detected in all the soil samples analyzed in this study (Table 1). Concentrations of PCDD/DFs and coplanar PCBs in soils from dumping sites were in the order of Philippines > Cambodia > India > Vietnam. In addition, concentrations of dioxins and related compounds in soils from dumping sites in Cambodia and India were notably higher than those from surrounding areas, and the levels of TEQs were comparable to or higher than those from urban, Industrial and incinerator surrounding areas in developed countries (3-5). This indicates that dioxins and related compounds have been secondarily formed by combustion of municipal wastes in dumping sites and coplanar PCBs have been leached out from dumped electric apparatuses. On the other hand, concentrations of PCDD/DFs in soils from dumping sites in Vietnam were relatively low and comparable to those from surrounding area, while the levels of these contaminants in the only one soil sample were notably high. This suggests that little PCDD/DFs have been recently formed in the dumping site of Vietnam, because municipal wastes have been covered with soils after dumping since 1998 and not burned by spontaneous combustion.

Compositions of PCDD/DFs in soils from dumping sites in Asian developing countries were notably different according to the levels of TEQs. In high-contaminated soils (>100 pg TEQs/g dry

Table 1. Mean and range concentartions (pg/g on dry wt.) of dioxins and related compounds in soils collected from dumping sites of municipal wastes and surrounding areas in Asian developing countries

	Cambodia		India		Vietnam		Philippines
	Dumping site (n =15)	Surrounding area (n =4) #	Dumping site (n =13)	Surrounding area (n =5)	Dumping site (n =9)	Surrounding area (n =1)	Dumping site (n =3)
TeCDDs	5600 (21-54000)	12 (0.5-42)	920 (68-6300)	0.55 (0.21-0.83)	1400 (4.6-12000)	5.0	6300 (3400-9300)
PeCDDs	7000 (12-73000)	12 (<0.01-38)	1000 (63-7500)	0.57 (0.28-0.89)	590 (3.3-5200)	5.5	6700 (4500-10000)
HxCDDs	5300 (18-50000)	16 (0.70-51)	1300 (110-8800)	1.1	510 (4.7-4400)	26	11000 (7100-18000)
HpCDDs	1200 (43-5800)	11 (3.2-30)	800 (300-3300)	3.4 (1.4-7.2)	210 (15-1500)	56	5800 (3600-7300)
OCDD	1400 (180-4400)	39 (6.5-74)	1900 (710-3600)	21 (9.9-53)	480 (75-1100)	270	12000 (7000-20000)
PCDDs	21000 (270-190000)	89 (26-230)	5900 (1500-29000)	26 (15-64)	3100 (100-24000)	360	42000 (30000-53000)
TeCDFs	4600 (25-23000)	18 (0.90-60)	490 (95-1600)	1.1 (0.19-1.7)	1500 (10-13000)	9.2	8700 (6000-11000)
PeCDFs	2800 (12-18000)	10 (<0.01-33)	330 (58-1300)	0.83 (0.25-1.3)	850 (2.8-7600)	1.0	4900 (3500-6000)
HxCDFs	1900 (9.8-10000)	9.1 (<0.01-27)	290 (54-1200)	1.0 (0.50-1.6)	490 (<0.01-4400)	<0.01	3300 (2500-4100)
HpCDFs	520 (6.6-3200)	3.4 (<0.04-12)	230 (50-1100)	1.4 (0.69-3.3)	160 (0.70-1400)	0.60	1800 (1400-2500)
OCDF	140 (5.0-840)	1.4 (<0.04-4.1)	110 (24-270)	1.9 (0.39-6.8)	38 (<0.04-320)	<0.04	500 (350-590)
PCDFs	10000 (59-53000)	42 (0.90-140)	1400 (410-5500)	6.2 (2.3-15)	2900 (15-26000)	11	19000 (14000-22000)
PCDD/DFs-TEQs	390 (1.4-1700)	1.9 (0.031-4.5)	47 (9.9-200)	0.23 (0.13-0.35)	110 (0.40-850)	1.0	520 (400-630)
non-*ortho* PCBs	1400 (98-4800)	0.90	570 (350-1100)	1.8 (1.2-2.6)	410 (19-2800)	6.4	2500 (1100-3900)
mono-*ortho* PCBs	8100 (590-24000)	10	6100 (1300-20000)	26 (12-52)	2200 (59-7100)	120	39000 (11000-83000)
Coplanar PCBs-TEQs	12 (1.1-27)	0.0016	5.0 (2.4-10)	0.022 (0.015-0.028)	7.3 (0.37-59)	0.096	26 (17-34)

coplanar PCBs (n =1)

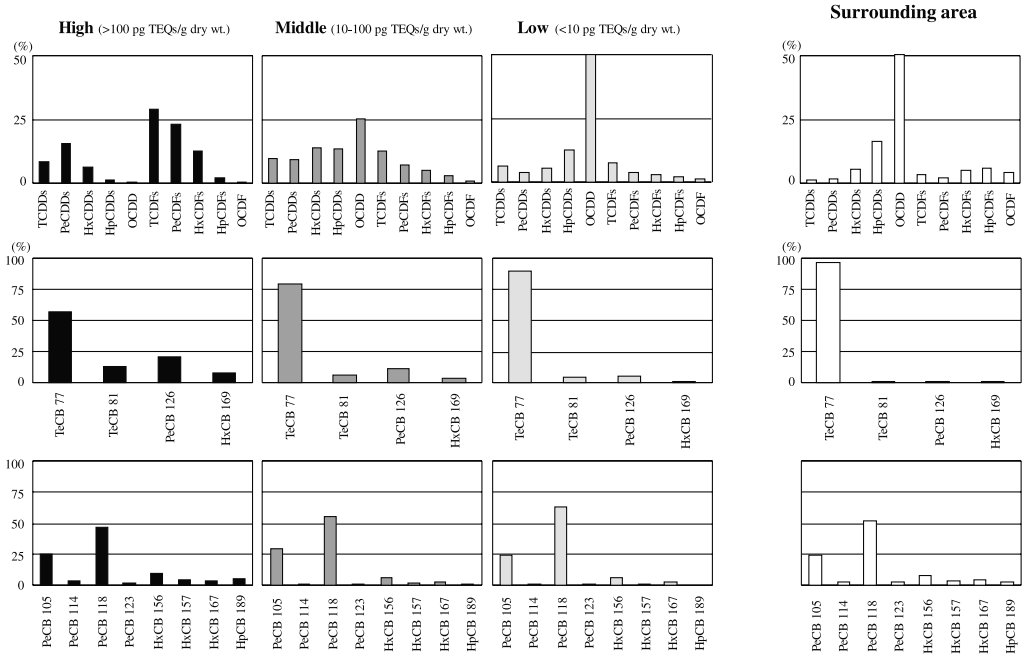

Fig. 1.
surrounding area in Asian developing countries.

wt.), the predominant homologues were tetra-, penta- and hexaCDD/DFs (Fig. 1). These homologues are generally detected in exhaust gas, fly and bottom ash from municipal waste incinerators (6), implying that these soils in dumping sites strongly reflect the pollution originated from combustion of wastes. On the other hand, in middle-contaminated soils (10-100 pg TEQs/g dry wt.), the dominant homologue was OCDD, and this trend was more dominant in low-contaminated soils (<10 pg TEQs/g dry wt.). According to the investigations of PCDD/DFs profiles in soils around municipal waste incinerators, the ratio of OCDD increased with the distance from incinerators, while levels of PCDD/DFs decreased (3, 7). This implies that the sites collected these soils, especially low-contaminated soils, were formed fewer amounts of PCDD/DFs under the incineration. OCDD was the most dominant in soils from surrounding areas. Similar patterns have also been reported in soils with background levels collected from developed countries (8, 9). Compositions of non-*ortho* PCBs in soils were also different according to the levels of TEQs, while those of mono-*ortho* PCBs were almost similar (Fig. 1). Relatively high levels of PeCB 126 and HxCB 169 were observed in high-contaminated soils. It is reported that these isomers are generally formed in the incineration process in municipal waste incinerators (6). This implies that PeCB 126 and HxCB 169 have been also formed by combustion of wastes in dumping sites and soils have been polluted by these contaminants.

Interestingly, the significant positive correlation were observed between concentrations of PCDD/DF homologues except OCDD, PeCB 126, HxCB 169 and copper in soils collected from dumping sites in Cambodia and India, indicating that copper in soils and /or municipal wastes catalyze reactions associated with formation of some dioxins and related compounds.

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References

1. Alcock, R. E., Jones, K. C. (1996) Dioxins in the environment: A review of trend data. *Environ. Sci. Technol.*, 30, 3133-3143.
2. Van den Berg, M., Brinbaum, L., Bosveld, A. T. C., Brunstrom, B., Cook, P., Feeley, M., Giesy, J. P., Hanberg, A., Hasegawa, R., Kennedy, S. W., Kubiak, T., Larsen, J. C., Rolaf van Leeuwen, F. X., Liem, A. K. D., Nolt, C., Peterson, R. E., Poellinger, L., Safe, S., Schrenk, D., Tillit, D., Tysklind, M., Younes, M., Waern, F., Zacharewski, T. (1998) Toxic equivalency factor (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. *Environ. Health. Perspect.*, 106, 775-792.
3. Domingo, J. L., Schuhmacher, M., Müller, L., Rivera, J., Granero, S., Llobet, J. M. (2000). Evaluating the environmental impact of an old municipal waste incinerator: PCDD/F levels in soil and vegetation samples. *J. Hazard. Mater.*, 76, 1-12.
4. Eljarrat, E., Caixach, J., Rivera, J. (2001). Levels of polychlorinated dibenzo-*p*-dioxins and dibenzofuans in soil samples from Spain. *Chemosphere*., 44, 1383-1387.
5. Fernandes, A. R., Timmis, R., Dawes, C. (1993). A survey of the dioxin content of soils in Walsall, U.K. *Organohalogen Compd*., 12, 191-194.
6. Sakai,S., Hatakawa,K., Takatsuki,H., Kawakami,I. (2001). Dioxin-like PCBs released from waste incineration and their deposition flux. *Environ. Sci. Technol*., 35, 3601-3607.
7. Lorber, M., Pinsky, P., Gehring, P., Braverman, C., Winters, D., Sovocool, W. (1998). Relationships between dioxins in soil, air, ash, and emissions from a municipal solid waste incinerator emitting large amounts of dioxins. *Chemosphere.*, 37, 2173-2197.
8. Rappe, C., Andersson, R., Bonner, M., Cooper, K., Fiedler, H., Howell, F., Kulp, S. E., Lau, C. (1997). PCDDs and PCDFs in soil and river sediment samples from a rural area in the united states of America. *Chemosphere*., 34, 1297-1314.
9. Rotard, W., Christmann, W., Knoth, W. (1994). Background levels of PCDD/F in soils of germany. *Chemosphere.*, 29, 2193-2200.