Levels of PCDDs, PCDFs and non-ortho coplanar PCBs in soil collected from high cancer-causing area close to Batch-type Municipal solid waste incinerator in Japan

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Introduction

Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) were first discovered in the fly ash and flue gases of municipal solid waste (MSW) incinerators[1], and since then have been detected in MSW incinerators of various countries, including Japan[2,3,4]. Recently, much importance has been attached to the problem of environmental pollution by dioxin analogues, such as PCDDs, PCDFs and non-ortho coplanar PCBs (Co-PCBs) released from MSW incinerators in Japan[5], because the number of MSW incinerators were 1841 in our country, and it occupied about 73% of total MSW incinerators in the world[6]. Therefore, it has been concerned for bad influence of health condition of residents near by MSW incinerators. In fact, high cancer-causing area close to Batch-type MSW incinerator has become of major interest lately; the residential area is located within 1.1 km on the leeward side from the incinerator in Shintone village of Ibaragi prefecture, and it is clear that cancer death rate for past 10 years in this area was 42% as extremely high rate. From the observation results which 2,3,7,8-TCDD have promortive activity for carcinogenesis[7,8], detailed analysis of dioxin analogues including 2,3,7,8-TCDD as the major isomer in soil around the incinerator is needed.

In the present work, we tried to survey the pollution levels by dioxin analogues including Co-PCBs in soil samples collected from its surrounding area of the incinerator at March in1996 and to prove the correlation with the results of epidemiological research and their pollution level in high cancer-causing area.

Experimental Methods

1) Collection and preparation of soil sample

As shown in Figure 1, the surface soil samples (depth until 2-3 cm) were collected from

61 points around MSW incinerator in Shintone village of Ibaragi prefecture, which are located at 50 km in the east of Tokyo, Japan. 52 samples on A~G lines except F line, were radially collected at approximately 200 m intervals within 2 km from the center of MSW incinerator, and 9 samples on F line cross to high cancer-causing area (X area) were also collected at 200 m intervals from East to West. Then, these samples were air-dried and screened by 30 mesh strainer.

2) Extraction and clean-up of dioxin analogue from soil sample

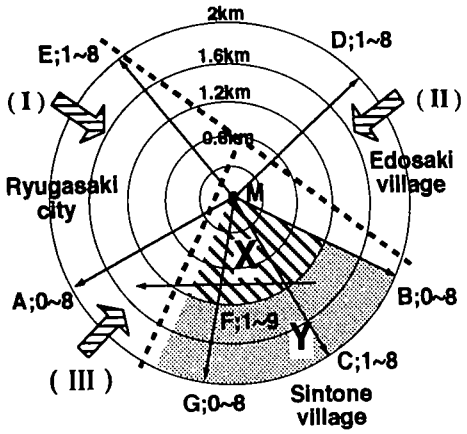
After spiking of internal standards (five $^{13}C_{12}$-PCDDs and five $^{13}C_{12}$-PCDFs, each 400 pg; three $^{13}C_{12}$-Co-PCBs, each 500 pg), 50 g of soil sample on each sampling point was extracted with 250 ml of toluene for 5 hr under reflux. The toluene extract was passed through a 1 μm glass-fiber filter to remove soil particles. Then, this filtrate was concentrated and replaced with 5 ml of n-hexane. The filtrate was cleaned up on a multi-layer column containing Na_2SO_4 (2.0 g), 10%(w/w) $AgNO_3$-silica (4.0 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 (170 ml). The eluate was concentrated to 5 ml, and separated into three fractions with successive eluents of 90 ml of n-hexane, 70 ml of 3% methylen chloride in n-hexane and 160 ml of 50% methylene chloride in n-hexane on an alumina (10 g, Merck, neutral active I) column. Third eluate containing PCDDs, PCDFs and Co-PCBs was concentrated up to 3ml, and then added 30 μl of n-decane as keeper solvent. The eluate was left for complete evaporation of n-hexane in room temperature and then adjusted to a volume of 30 μl with n-decane. Finally, 30 μl of eluate as purified sample was used for analysis of gas chromatograph (GC)- mass spectrometer (MS).

Determination of dioxin analogue in the purified sample by GC-MS analysis

The purified sample was analyzed on J&W DB-5 (30 m x 0.32 mm, 0.20 μm film thickness), {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 Co-PCBs, {held for 1 min at 120°C at 20°C/min, to 260°C at 4°C/min and to 310°C at 20°C/min} for hepta- and octachlorinated PCDDs and PCDFs, and on Supelco 2331 (60 m x 0.32 mm, 0.20 μm film thickness), {programed from 150°C to 180°C at 20°C/min and to 250°C at 3 min, and held for 29 min} for tetra- through hexachlorinated PCDDs and PCDFs in an electron impact-single ion monitoring mode at a resolution of 8000 using Hewlett Packard 5890J GC-JEOL SX-102 MS. The concentrations of PCDDs, PCDFs and Co-PCBs were corrected with the recoveries of their respective internal standards. Finally, to compare the toxic level by PCDDs, PCDFs and Co-PCBs in analyzed soil samples, the values of 2,3,7,8-TCDD toxic equivalent quantity (TEQ) were calculated for PCDDs and PCDFs using international 2,3,7,8-TCDD Toxicity Equivalence Factors (I-TEFs)[9] and for Co-PCBs using TEFs[10].

Results and discussion

The MSW incinerator having disposable capacity of 60 tons/day (maximum 21,900 tons/year; if the disposable operation was done everyday), was built in 1971, and it was enough to dispose the wastes from 60,000 people in Shintone village and Ryugasaki city at first time. However, by a rapid increase of the wastes from the residents in the district, a



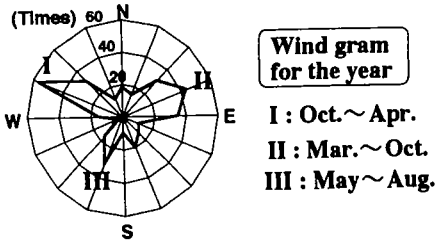


Figure 1
Map of soil sampling points on A-G lines, and high cancer-causing area (X area) and other area (Y area) epidemiological surveyed around Batch-type MSW incinerator

M; MSW incinerator
..... ; Local border line

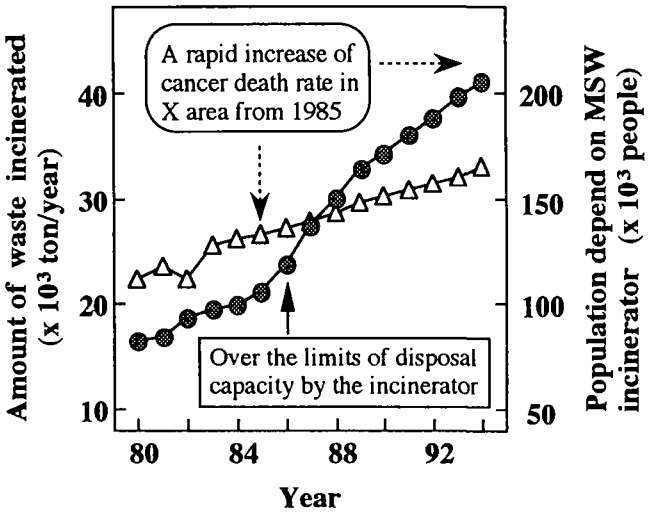


Figure 2
Alterations (1980-1994) of amounts of inflammable solid waste incinerated (●) and popolation depend on Batch-type MSW incinerator (△) in Shintone village of Ibaragi prefecture, Japan

Table 1 Comparison of cancer death rate of the residents (1985-1995) in high cancer-causing area (X area)[a] and other area (Y area)[b] on the leeward side from MSW incinerator in Shintone village of ibaragi prefecture[c], Japan[d]

Area	Total number of death	Number of death from cancer	Cancer death rate (%)
X	57	24	42
Y	167	34	20

a) X area is located within 1.1 km in the direction of south from MSW incinerator.
b) Y area is located from 1.1 km to 2.0 km in the direction of south from MSW incinerator.
c), d) Cancer death rates in Ibaragi prefecture and Japan were 25% and 28%, respectively.

serious social problem accompanying dioxin pollution, has been occurred after 1980's; although it was completely over the limits of disposable capacity by the incinerator from 1986, the operation with incomplete combustion is being continued (Figure 2). Further, from the result of survey on the cancer death rates in the X area (0-1.1 km) and the Y area (1.1-2 km) on the leeward side through the year, it was recognized that its death rate (1985 -1995) in the X area was 42%, comparison with that (20%) in the Y area (Table 1). On the basis of the above result, the analysis of pollution levels by dioxin analogues in 61 soil samples collected from its surrounding area of the incinerator was performed.

Figure 3 shows the comparisons of the total concentration of PCDDs, PCDFs and Co-PCBs and their total concentration calculated as 2,3,7,8-chlorinated substituted PCDDs (TEQ concentration) in soil samples on G, B and E lines. The total concentration of dioxin analogues in all soil samples on G line of leeward side were heavily polluted with the levels of 5303 to 32167 pg/g on the average of 13934 pg/g (Fig. 3a). Further, it was observed that fly ash with dioxin analogues fell on the two specific area on G line, indicating sampling point of G-0 and G-2 (0.2-0.5 km), and sampling point of G-6 and G-7 (1.6-1.8 km). The interesting phenomenon suggested that the difference of particle size in fly ash may depend on diffusion length in the atmosphere. Thus, it was estimated that the dioxin analogues formed on large or fine particles in fly ash were transported by the blowing wind, and fallen on the localized area by the weight of particle itself. With respect to TEQ concentration, that in the samples of G-0 and G-1 were 252 and 211 pg/g, respectively. This incredible pollution levels indicated that the health of residents near sampling points of G-0 and G-1 are extremely in a state of danger. Then, the soil samples of B-1, B-2, B-3 and B-4 except B-0 within 1.2 km on B line, were also highly contaminated with dioxin analogues in a range of 10844 to 37963 pg/g, whereas other samples over 1.2 km were not (Fig. 3b). It is not easy to directly relate with the high contamination by dioxin analogues and their carcinogenesis, however, the analytical results of G and B line suggests that other carcinogenic substances, such as polycyclic aromatic hydrocarbons or heavy metals containing the fly ash or flue gases may also fallen on the X area[11,12]. On the other hand, it was clear that all samples on E line of the windward side except the nearest E-0 sampling point were little contamination (Fig. 3c).

As shown in Figure 4, the real situation of surrounding soil pollution by dioxin analogues released from the MSW incinerator was illustrated. Among 61 soil samples analyzed, the total concentration over 2000 pg/g was observed in 45 samples (78.8%), and the TEQ concentration over 10 pg/g was observed in 39 samples (63.6%). Therefore, it was revealed that the soil in surveyed area was widely polluted by dioxin analogues. In addition, the pollution level of the X area and the Y area was compared; the ratio of high contamination over 5000 pg/g was 63.2 % in the soil samples of the X area, whereas that was 38.5% in the soil samples of the Y area (Fig. 4a). Similarly, the ratio of high contamination over 30 pg TEQ/g was 26.3 % in the soil samples of the X area, whereas that was 15.3% in the soil samples of the Y area (Fig. 4b).

From all results, it could be demonstrated that the results of epidemiological research and the pollution level of the X area as high cancer-causing area by dioxin analogues was well correlated.

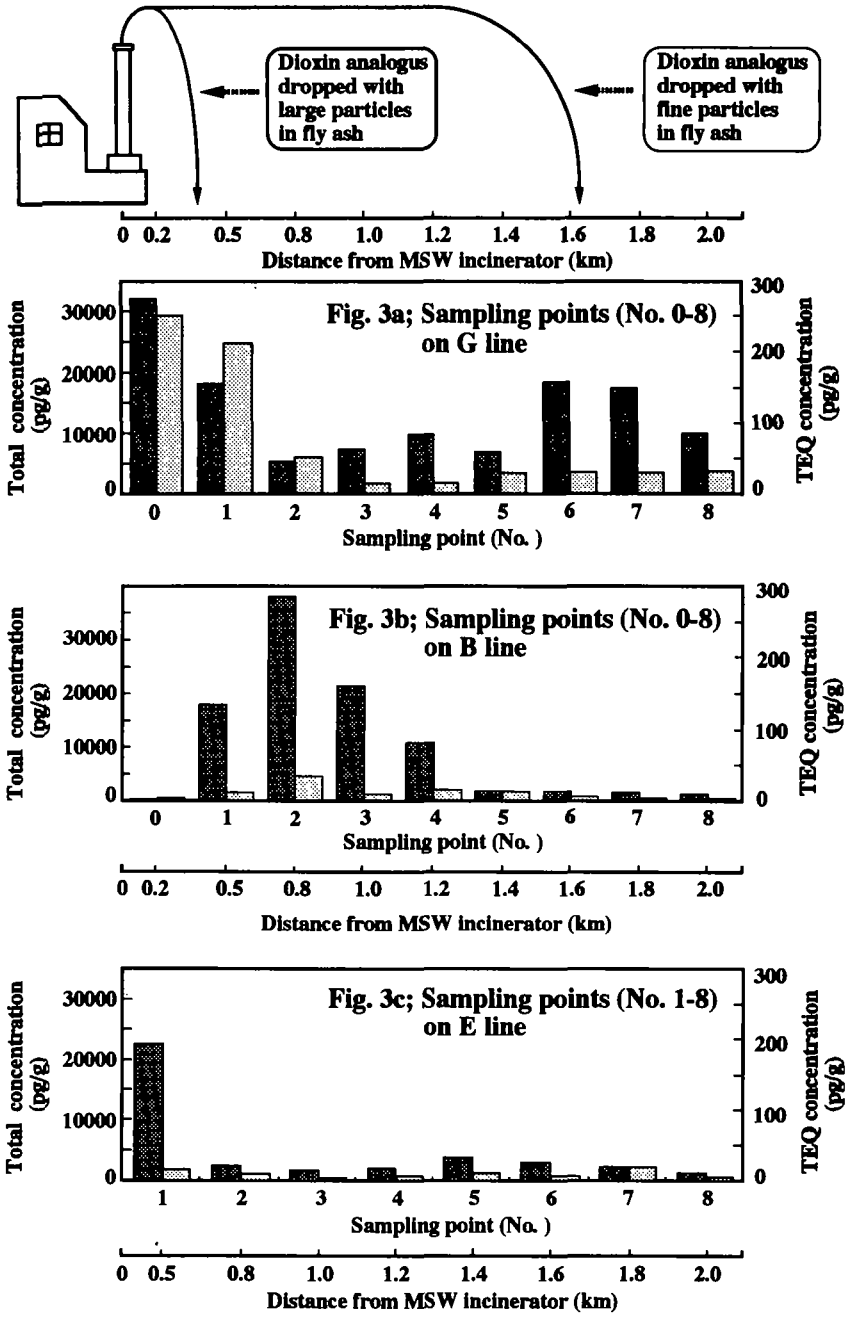


Figure 3 Comparisons of total concentration of PCDDs, PCDFs and Co-PCBs (■) and their TEQ concentration (□) in soil samples on G line (Fig. 3a), B line (Fig. 3b) and E line (Fig. 3c) around Batch-type MSW incineratorin Shintone village of Ibaragi prefecture, Japan

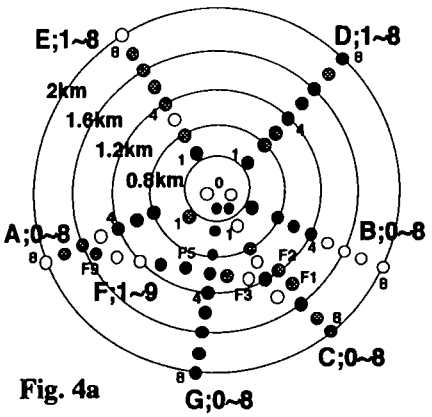


Fig. 4a

○: < 2000, ◉: 2000~5000, ●: > 5000 (pg /g)

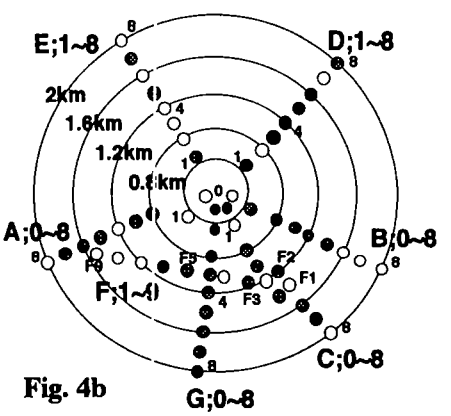


Fig. 4b

○: < 10, ◉: 10~30, ●: > 30 (pg TEQ/g)

Figure 4 Real situation of surrounding soil pollution (Fig. 4a; pg/g, Fig.4b; pg TEQ/g) by PCDDs, PCDFs and Co-PCBs released from Batch-type MSW incinerator in Sintone village of Ibaragi prefecture, Japan

Acknowledgments

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Literature cited

1 Oile, K.; Vermeulen, P.L.; Hutzinger O. Chemosphere. **1977**, 6, 455-459.
2 Rappe, C.; Anderson, R.; Bonner, M.S.; Cooper, K.R.; Fiedler, H.; Howell, F.G.;
3 Lau, C. Organohalogen Compounds. **1996**, 11, 245-248.
4 Miyata, H.; Aozasa, O.; Mase, Y.; Ohta, S; Khono, S.; Asada, S. Chemosphere. **1994**, 29, 9-11.
5 Sakai, S.; Hiraoka, M.; Takeda, N.; Shiozaki, K. Organohalogen Compounds. **1993**, 11, 245-248.
6 Hiraoka, M; Okajima, S. Organohalogen Compounds. **1994**, 19, 275-291.
7 Clark, G.C.; Taylor, M.J.; Tritcher, A.M.; Luicher, G.W. Toxicol. Appl. Pharmacol. **1991**, 111, 422-431.
8 Pitot, H,C.; Sirica, A.E. Biochem. Biophys. Acta. **1994**, 605, 101-215.
9 Kutz, F.W.; Barnes, D.C.; Bottimore, D.P.; Greim, H.; Bretthauer, E.W. Chemosphere. **1990**, 20, 751-757.
10 Ahlborg, U.G.; Becking, G.C.; Birnbaum, L.S.; Brouwer, A.; Derks, H.J.G.M.; Freeley, M; Golor, G.; Hanberg, A.; Larsen, J.C.; Liem, A.K.D.; Safe, S.H.; Schlatter, C.; Warn, F.; Younes, M.; Yrjanheikki, E. Chemosphere. **1994**, 28, 1049-1057.
11 Takasuga, T.; Inoue, T.; Ohi, E.,; Ireland, P.; Suzuki, T.; Takeda, N. Organohalogen Compounds. **1994**, 19, 41-44.
12 Stieglitz, L.; Zwick, G.; Beck, J.; Roth, W.; Vogg, H. Chemosphere. **1989**, 18, 1219-1226.