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Survey on Levels of PCDDs, PCDFs, and Non-Ortho Co-PCBs in Soil and Sediment from a High Cancer Area near a Batch-Type Municipal Solid Waste Incinerator in Japan

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Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) were first discovered in the fly ash and flue gases of municipal solid waste (MSW) incinerators (Olie et al. 1977). Since then PCDDs and PCDFs have been detected in Municipal Solid Waste (MSW) incinerators in various countries including Japan (Lau 1996; Miyata et al. 1994; Schuhmucher et al. 1997). 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 (Miyata et al. 1997; Nakao et al. 1997). This is because the number of MSW incinerators was 1841, about 73% of all MSW incinerators in the world (Hiraoka and Okajima 1994). As a result, the amount of waste incinerated was over forty million tons per year. Furthermore, it has been estimated that similar amounts of industrial waste are incinerated. Therefore, residents around such incinerators are concerned about the adverse effects on their health. In fact, Shintone Village as the high cancer death area on leeward side from the Batch-type MSW incinerator operated by Ryugasaki City in Ibaraki Prefecture, located approximately 50 km north-east of Tokyo, is of major interest lately. The number of inhabitant in Shintone Village was about 10,000, and many people in the small village have been engaged in farming. According to a survey, between 1985 and 1995, the death number of residential area X and Y as shown in Figure 1, were 57 and 167, respectively. Among 224 dead people in both area, the cancer death number in the X area, within 1.1 km downwind of the incinerator, was 24 (42 %) for 57 residents as total number of deaths, compared to 34 (20 %) in the Y area. Over two times for cancer death rate in the Y area was observed in the X area, referred to 28% as the average cancer death rate in Japan. Because 2,3,7,8-TCDD had promotive activity for carcinogenesis (Clark et al. 1991;Lai et al. 1997), a detailed analysis of dioxin analogues represented by 2,3,7,8-TCDD in environmental samples around this incinerator is therefore needed. We investigated the pollution levels by dioxin analogues including non-ortho coplanar PCBs in soil and sediment samples collected from the incinerator's surrounding area.

MATERIALS AND METHODS.

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

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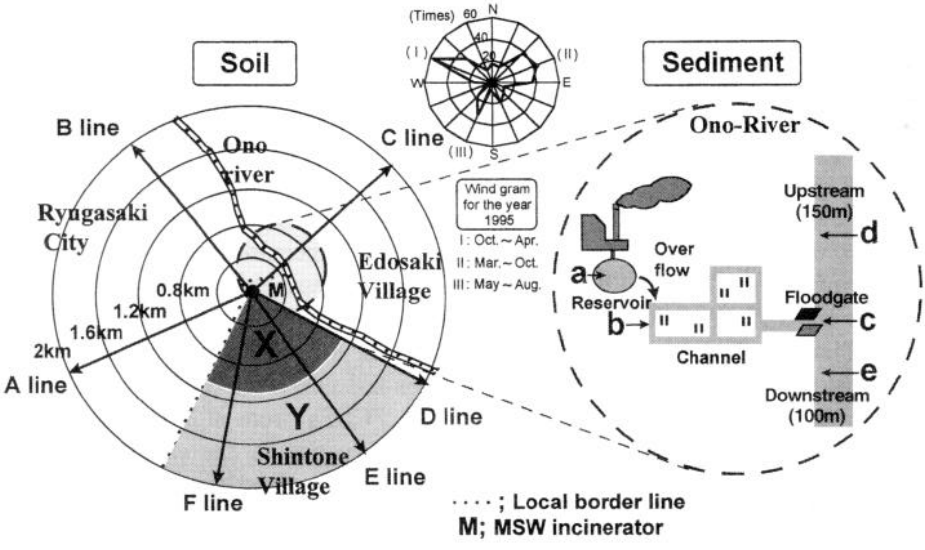

Figure 1. Locations of sampling points of soil (A-G line) and sediment (a-e) around the MSW incinerator

52 points around the MSW incinerator in Shintone Village, Ibaraki Prefecture of Japan in March in 1996. 52 samples of A-F lines were radially collected at 0.2, 0.5, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8 and 2.0 km from the center of the MSW incinerator. Similarily, surface sediment samples were collected from five points: the reservoir pond in the incinerator (a), narrow channels from the pond to the Ono River (b) and the Ono River 500 m east of the incinerator (c, floodgate, d, 150 m upstream from the floodgate, e, 100 m downstream from the floodgate). These samples were completely dried and screened by a 30-mesh strainer.

To purify the dioxin analogues, after spiking of internal standards (five $^{13}C_{12}$-PCDDs and five $^{13}C_{12}$-PCDFs, each 400 pg, and three non-ortho $^{13}C_{12}$-Co-PCBs, each 500 pg), 50 g of soil sample from 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_2SO4-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 of successive eluents of 90 ml of n-hexane, 70 ml of 3% methylene chloride in n-hexane and 160 ml of 50% methylene chloride in n-hexane on an alumina (10 g, Merck, neutral activity I) column. The third eluate containing PCDDs, PCDFs and Co-PCBs was concentrated to 3ml. Then, 30 µl of n-decane was added as a keeper solvent. The eluate was left to completely evaporate n-hexane at room temperature, then adjusted to a volume of 30 µl with n-decane. Finally, 30 µl of the eluate as the purified sample was used for analysis by gas chromatography (GC) and mass spectrometry (MS).

To determine the dioxin analogue 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). For Co-PCBs, which was held for 1 min at 140 °C, then programmed to 220 °C at a 20 °C/min increase, then to 310 °C at an 8 °C /min increase, and held for 4 min; held for 1 min at 120 °C at 20 °C /min, then programmed to 260 °C at a 4 °C /min increase, then to 310 °C at a 20 °C /min increase for hepta- and octachlorinated PCDDs and PCDFs, and on Supelco 2331 (60 m x 0.32 mm, 0.20 µm film thickness), (programmed from 150 °C to 180 °C at a 20 °C /min increase and to 250 °C at a 3 min increase, 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 detection limits for tetra- through hexachlorinated PCDDs, PCDFs and non-ortho coplanar PCBs and hepta- through octachlorinated PCDDs and PCDFs were 0.2 and 1.0 pg/g, respectively. Samples, which exhibited the recoveries in the range of 50 % to120 % for their respective internal standards, were used for data collection. Finally, to compare the toxic level of PCDDs, PCDFs and Co-PCBs in the analyzed 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 as I-TEFs (Kutz et al. 1990) and for non-ortho Co-PCBs using TEFs (Ahlborg et al. 1994)

RESULTS AND DISCUSSION

The MSW incinerator built in 1971, has a disposable capacity of 60 tons/day. It was enough to dispose the waste from residents in Shintone, Village and Ryugasaki City during the 1970's. However, because of a rapid increase of wastes due to an increase in population, a serious social problem accompanying dioxin pollution has occurred after the first half of 1980's. Although the incinerator's capacity has been exceeded, the operation of incomplete combustion continues. It was suggested that the dioxin analogues from the contaminated environment may have caused adverse effects to many residents. Therefore, analysis of pollution levels by dioxin analogues in 52 soil samples around the Shirotori MSW incinerator was performed. Figure 2 shows the comparisons of the total concentration of PCDDs, PCDFs and Co-PCBs and their TEQ concentrations in soil samples on A-F lines. It was clear that all samples on B line of the windward side, except the nearest the B-l sampling point, had little contamination. However, soil samples from a wide area on C, D and F lines were highly contaminated. Moreover, the total concentration of dioxin analogues in all soil samples on the F line of the leeward side through one year were polluted, with levels between 5.3 and 32.2 ng/g,, averaging 13.9 ng/g.. Furthermore, fly ash with dioxin analogues fell on two specific areas of the F line, indicating sampling points of F-l and F-2 (0.2-0.5 km), and sampling points of F-7 and F-8 (1.6-1.8 km). This 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 dioxin analogues formed on large or fine particles in fly ash were transported by blowing wind, falling on the localized area by the weight of the particle itself.

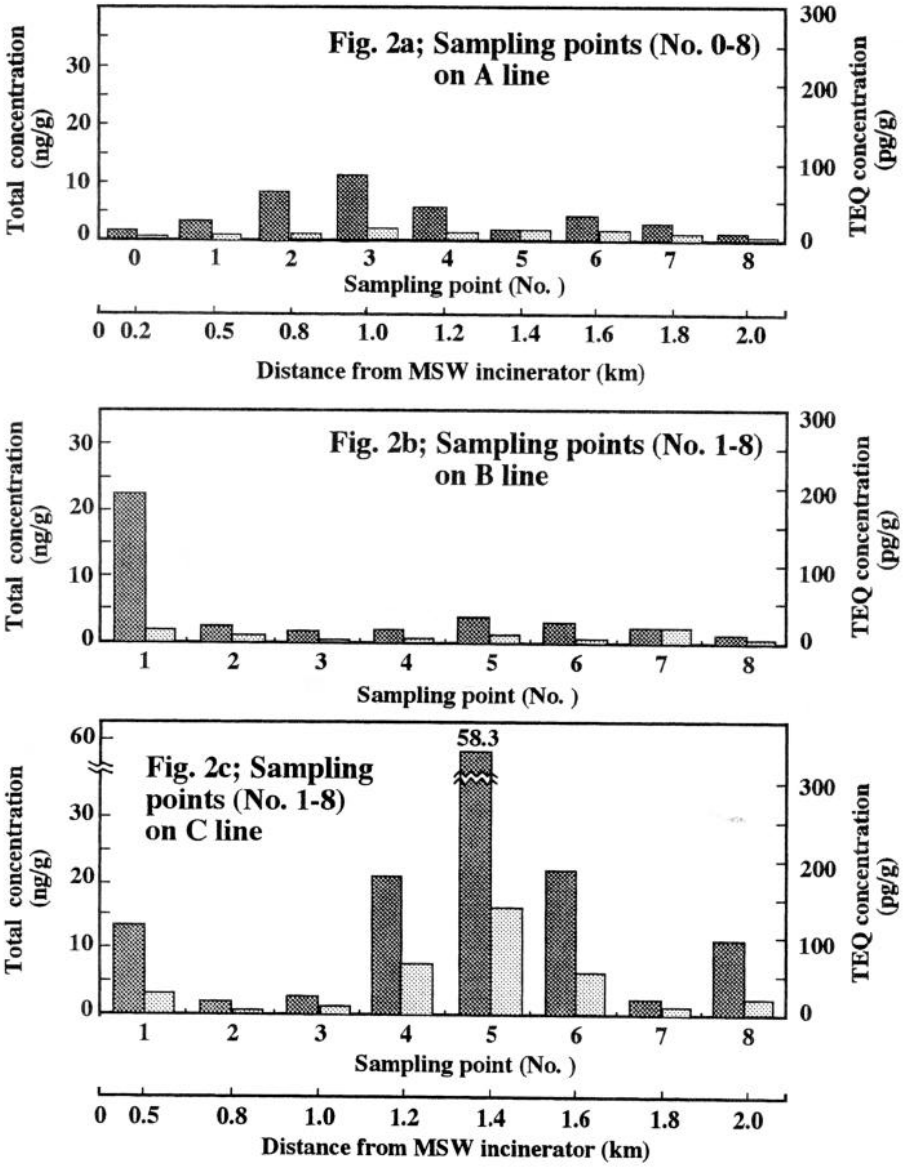

Figure 2. Comparisons of total concentration of PCDDs, PCDFs and Co-PCBs (▩) and their TEQ concentration (□) in soil samples on A-F line around Batch-type MSW incinerator in Shintone Village of Ibaragi prefecture, Japan

A similar phenomenon was observed in samples on C and E lines. With respect to the TEQ concentration, samples of F-1 and F-2 was 252 and 211 pg/g, respectively. These high pollution levels indicate that the health of the residents nears the F-1 and F-2 sampling points is an extreme state of danger. However, the total concentration in the soil samples of D-1~D-4, except D-0, within 1.2 km on the D line, was also contaminated with dioxin analogues, in a range between 10.8

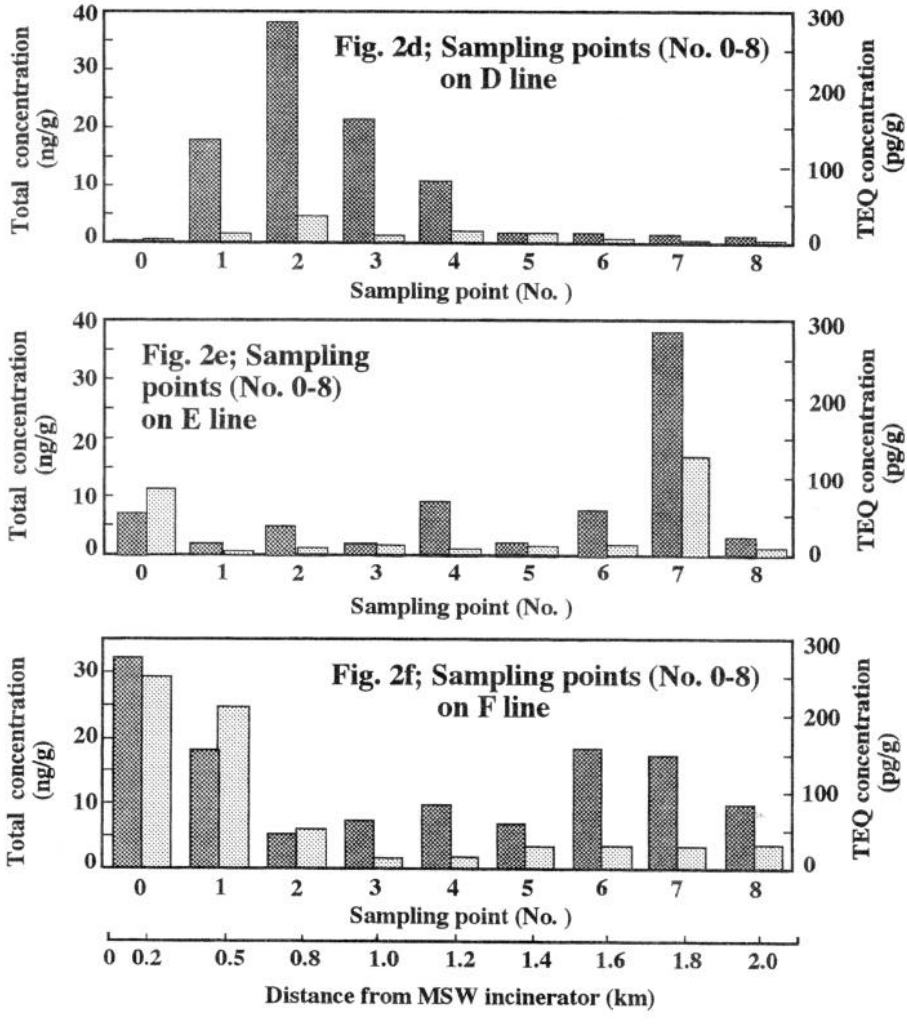

Figure 2 (cont.) Comparisons of total concentration of PCDDs, PCDFs and Co-PCBs (▩) and their TEQ concentration (▨) in soil samples on A-F line around Batch-type MSW incinerator in Shintone Village of Ibaragi prefecture, Japan

and 38.0 ng/g, whereas other samples over 1.2 km were not, showing a low TEQ level in all samples. Therefore, when we evaluate the contamination level in soil samples around the MSW incinerator's influence of wind direction and complex factors such the geographical features and the stability of dioxin analogues in the environment must be considered. The surrounding soil pollution by dioxin analogues released from the MSW incinerator is illustrated in Fig.3. Among the 52 soil samples analyzed, 39(75%) had a total concentration over 2000 pg/g, and 33 (63%) had a TEQ concentration over 10 pg/g. TEQ levels in soil samples of rural area in Japan such as Ryugasaki City and Shintone Village are below 5 pg/g

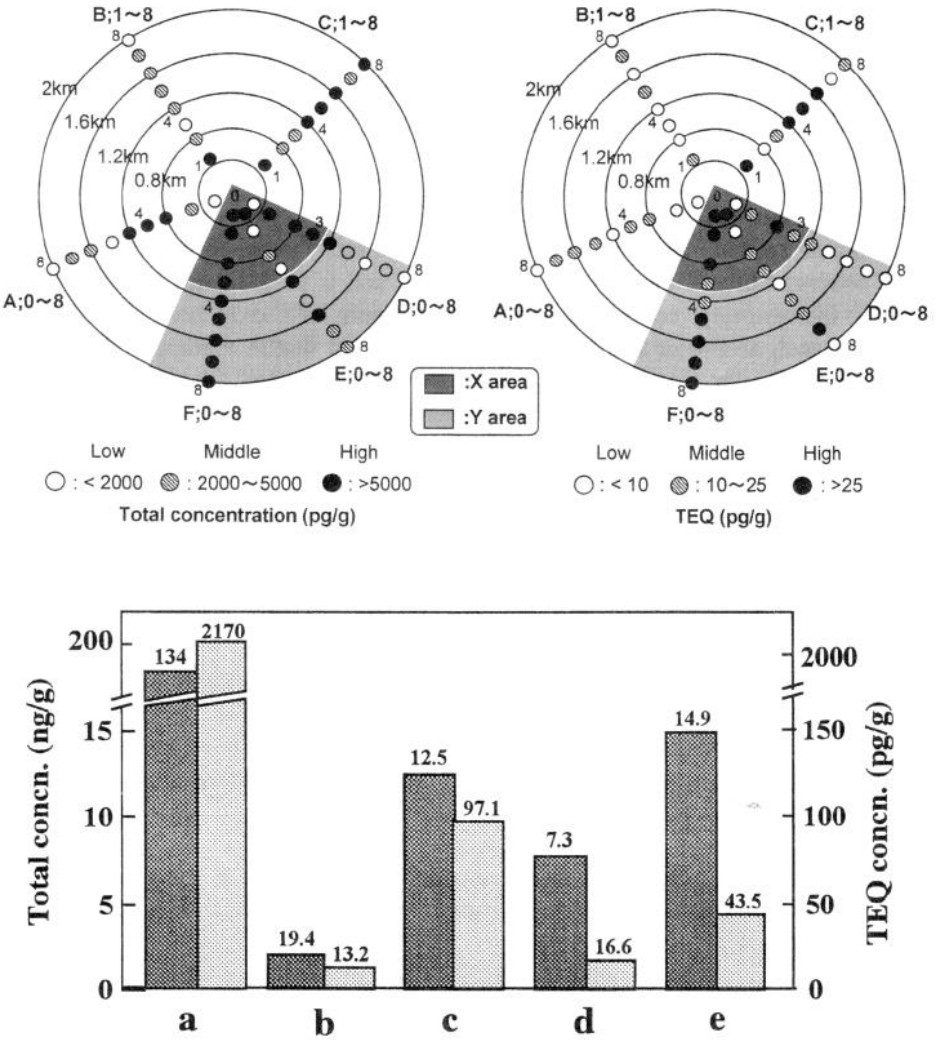

Figure 4. Total concentration (ng/g) of PCDDs, PCDFs and non-ortho Co-PCBs, and their TEQ concentration (pg/g) in a-e sediments around MSW incinerator

(Ohta et al. 1997). Therefore, it was shown that soil in the surveyed area was widely polluted by dioxin analogues. In addition, the average TEQ level in the 12 samples from the X area and the 15 samples from the Y area were 59.0 and 23.4 pg/g, respectively. Thus, 2.5 times more contamination by dioxin analogues was observed in the X area, a similar the cancer death rates in this district. It is not easy to directly correlate contamination by dioxin analogues and carcinogenesis.

However, it has been reported that other carcinogenic substances such as polycyclic aromatic hydrocarbons (PAHs) or heavy metals were recognized in the

fly ash or flue gases from MSW incinerator (Takasuga et al.1994; Stieglitz et al. 1989). In practice, it was also noted that the high contamination in these samples by various PAHs, e.a., benzo(a)pyrene(data not shown). Therefore, the high cancer death rate in this district may be due to the interaction between dioxin analogues and other chemicals such as PAHs and heavy metals. Figure 4 shows the total concentration of PCDDs, PCDFs and Co-PCBs and their TEQ concentrations in sediments from points a-e near the MSW incinerator (as shown in Figure1). A remarkable contamination in sediments from the reservior pond in the incinerator was observed total concentration of 184 ng/g and a TEQ concentration of 2.14 ng/g.. Interestingly, comparing the isomer pattern of dioxin analogues in soil samples such as F-O or F-l near the incinerator and that in a-point sediment, an extremely similar pattern was noted in both samples (data not shown). Furthermore, the pollution level of sediment from the e-point downstream from the floodgate on the Ono River, was higher than that from the d-point upstream from the floodgate. This observation supports that sediments in the Ono River were also contaminated from wastewater from the reservoir pond, not only through fly ash and flue gasses. The reason why the levels of b-point sediment collected from the narrow channel from the incinerator to the Ono River were low was because the residents periodically removed the accumulated sediment in channel.

It is difficult to simply conclude a relationship between a high cancer death rate and the pollution level by dioxin analogues in the X area. Evidence shows residents in the area leeward to the batch-type incinerator have high health, compared to residents in other areas. Further work is planned to analyze the contamination by dioxin analogues in the blood of residents.

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