DECOMPOSITION OF DIOXINS IN SOIL OF PADDY FIELDS AND SOIL OF MUNICIPAL SOLID WASTE INCINERATOR SURROUNDINGS USING SUNLIGHT AND HYDROGEN PEROXIDE

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Abstract

A large amount of dioxins are stocked in Japanese environment such as paddy soils and surrounding ones of solid waste incinerators. To reduce these stocks of dioxins is necessary to reduce the risk of them to human and ecosystem exposure. In this study, dioxins in paddy soil and incinerator surrounding soil were tried to decompose. One gram of the sample soil was suspended in 300 ml of hydrogen peroxide (H_2O_2) solution. August's sunlight was irradiated in the former case for 9 hours, and xenon light was irradiated in the latter case for the same hours. As a result, the TEQ in the former soil decreased by 98% at H_2O_2 12%. In the latter case, it had exceeded the Japanese environmental criteria for soil (1,000pg/g), but decreased by 81% at 12% H_2O_2 to well below 250pg/g in which a governmental organization was requested to start to investigation.

Introduction

Dioxins once produced by human activities persist in various places of Japan such as paddy fields, surroundings of solid waste incinerators, sediments in river mouths and so forth. In paddy fields, dioxins were introduced in the past unintentionally as byproducts of the herbicides pentachlorophenol (PCP) and chloronitrophen (CNP) and they continue to remain there nationwide[2)]. Soils in surroundings of many solid waste incinerators are heavily polluted by dioxins produced during combustion and released as exhaust. To minimize the amount of these dioxin loads in the environment artificially is essential to minimize dioxin exposure of human and ecosystem.

Heat, electric or biological treatment has been reported to decrease the amount of dioxins in soil. However, these treatments are energy and time consuming. Therefore, in this study, the dioxin decomposition by summertime sunlight irradiation or a xenon lamp one with or without hydrogen peroxide (H_20_2) was studied to find appropriate inexpensive and environmentally safe ways for the dioxin decomposition.

Materials and Methods

Materials

Two samples were used. One is paddy soil which was collected in Noshiro City in Akita Prefecture in 2000, which is in the north part of Honsyu Island of Japan, and in which tetra-, penta- and octa-chlorinated debenzo dioxins were predominant (Figure 1). After the collection, the samples were

Table 1. Experimental Structure

Sample	Experiment Date	Stir	H_2O_2 (%)	Light Source	Irradiation Time
Paddy Soil	August in 2008	Stir	0, 1,3 and 12	Sun Light	36 hours
	September in 2008	Stir			
		No Stir			
Soil of a Solid Waste Incinerator Surroundings		Stir	0, 3 and12	xenon Lamp	

air-dried at room temperature and sieved through a 1 mm alum sieve. The other was soil of incinerator surroundings, in which polychlorinated debenzofrans were predominant and the TEQ exceeded the Japanese environmental criteria for soil (1,000pg/g). As the percentage of dioxin-like PCBs was only 0.1 % of the TEQ in paddy field soil and 0.7 % of it in incinerator surroundings soil, it was not considered in this study.

Experimental Method

Experimental conditions are shown in Table 1. It is well known that sunlight does not penetrate deep into soil layers. Therefore, in this study, tests using soil slurry was designed. One gram of paddy soil was put in a quartz glass beaker. Then, 300 ml of H_2O_2 solution, which concentration was 0, 1, 3 or 12%, was added. These four beakers were placed on the roof of a building of Niigata University and exposed to sunlight for 3 days from 6:00 to 18:00 with stirring using a magnetic stirrer (540rpm). In the case of surrounding soil of municipal solid waste incinerator, one gram

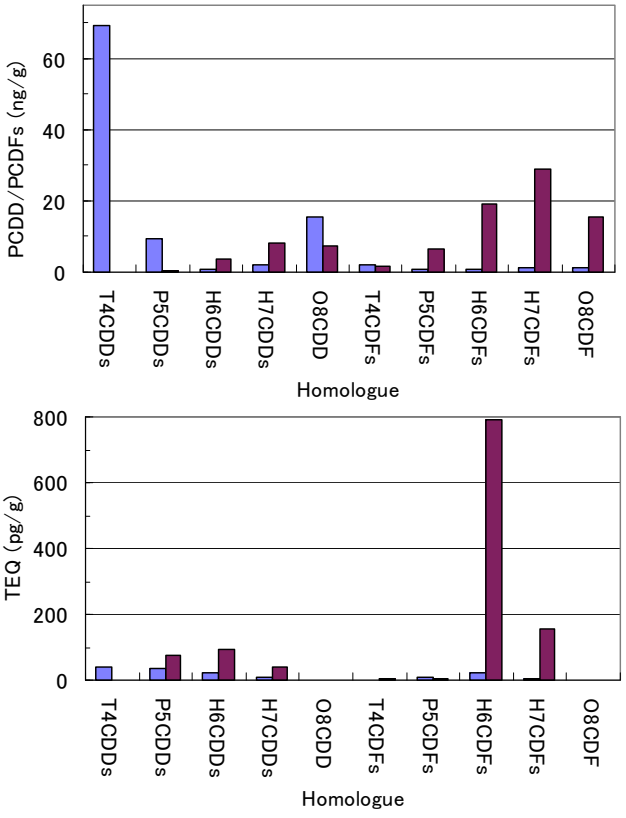

Figure 1. Homologue Composition of the Samples (above: Total Dioxin, below: TEQ)

of the soil was put in a quartz glass beaker. Then, 300 ml of H_2O_2, which concentration was 0, 3 or 12%, was added. Then the quartz beakers were exposed to a xenon lamp irradiation (Ushio UXL-500SX) for 36 hours, with stirring using a jar tester (120rpm).

For the measurement of solar radiation, PCM-01 (PREDE Co., Ltd,) was used for visible light (401-2,800 nm). For ultraviolet A (UVA, 321-400nm) and B (UVB, 280-320nm), Solar meter MODEL 5.0 and MODEL 6.0 (Solartec Co., Ltd) were used respectively. For the measurement of H_2O_2 concentration, H_2O_2 meter (Pocket PAL-39S, ATAGO Co., Ltd) was used. Whenever H_2O_2 concentration decreased, H_2O_2 was added manually to maintain the initial H_2O_2 concentration.

Dioxins Analysis

After the irradiation, the samples were filtered through a glass filter paper with a pore size of 1.0 µm. To the filtrate and the residue on the filter paper, ^{13}C-labeled internal standards were added. Then, the filtrate was extracted using dichloromethane. The filter paper and the residue on it were extracted using toluene by a Soxhlet extractor. Each extract was concentrated, then mixed. The mixture was treated with concentrated sulfuric acid and purified by filtration through a silica gel column and by filtration through an active carbon-impregnated silica gel column.

The eluate which contained the final PCDD/PCDFs was concentrated to 100 µl and analyzed for tetra- to octa-chlorinated PCDD/PCDFs by using a high-resolution gas chromatograph high-resolution mass spectrometer (HRGC-HRMS; Hewlett Packard HP 6890/JEOL JMS-700). The HRMS

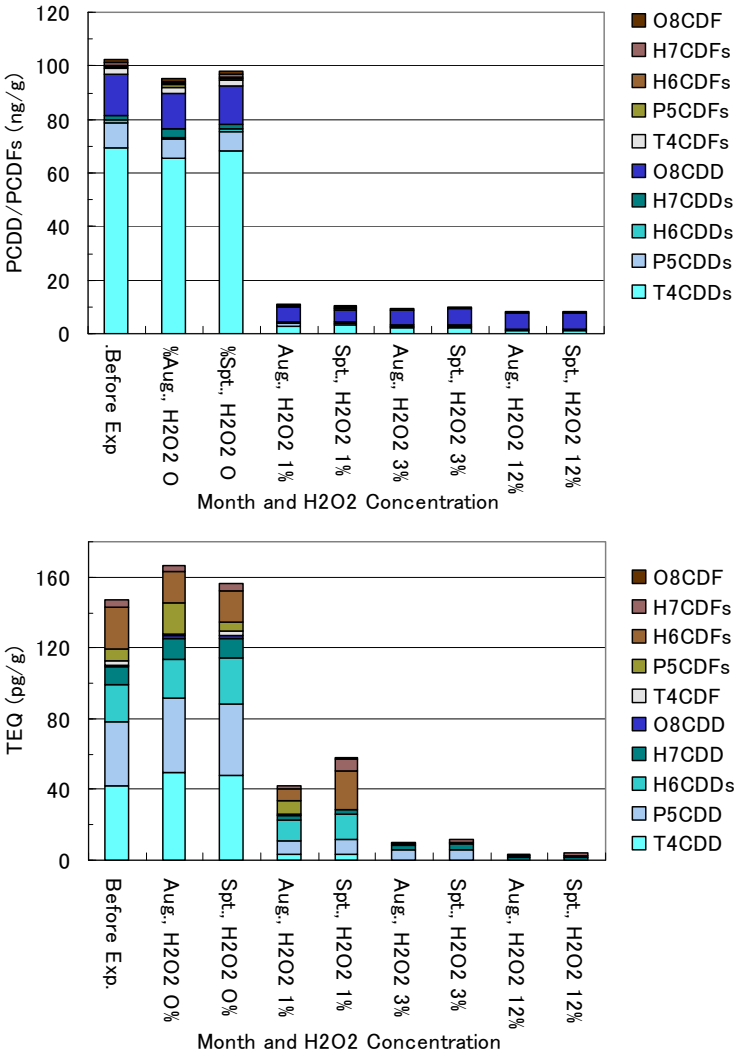

Figure 2. Effects of August and September sunlight and H_2O_2 concentration (above: Total Dioxin, below: TEQ).

was operated in the electron impact mode and in the selected ion monitoring mode at a resolution of R > 10,000. Both DB5 (5% phenyl and 95% methyl polysiloxane, J&W Scientific) and DB-17 (50% phenyl and 50% methyl polysiloxane, J&W Scientific) were used as the capillary columns. PCDD/PCDFs were quantified by the internal standard method, using ^{13}C-labeled dioxins as the standards. For toxicity equivalent quantity (TEQ) calculation, the World Health Organization toxicity equivalent factor (WHO 1998-TEF) was used.

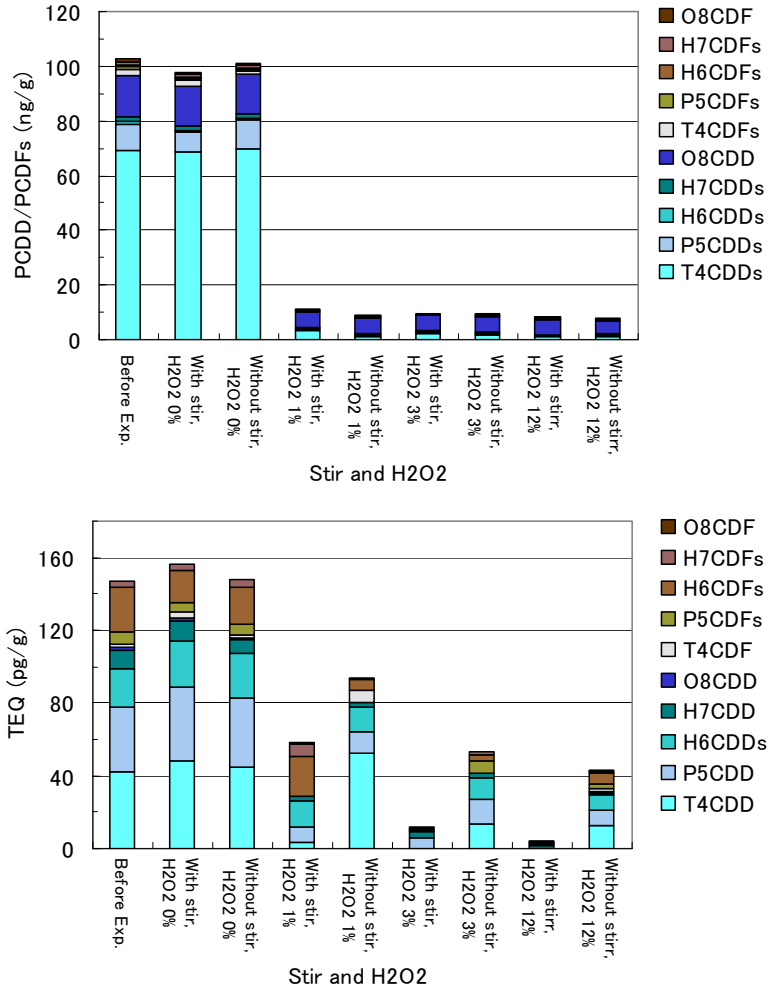

Figure 3. Effects of stirring and H_2O_2 concentration in September (above: Total Dioxin, below: TEQ).

Results and Discussion

Radiation Amounts

The average radiation amount of the xenon light, sunlight in August and that in September were 1,130W/㎡, 479W/㎡, 440W/㎡ in visible range; 135W/㎡, 29W/㎡, 28W/㎡ in UVA range; 65W/㎡, 2W/㎡, 1.6W/㎡ in UVB range, respectively. The radiation amount of xenon light was much larger than those of sunlight. In sunlight radiation, there was little difference between August and September.

Results of Paddy Soil

Figure 2 shows the effects of August and September sunlight and H_2O_2 on the dioxin decomposition. There were little differences of results between in August and in September. The total PCDD/PCDFs concentration decreased only a little without H_2O_2. However, when H_2O_2 was added at 1, 3 or 12%, it decreased about by 90%. In contrast, The TEQ increased only a little without H_2O_2. However, it decreased as H_2O_2 concentration increased. The TEQt decreased by 65 % at H_2O_2 1%, 92% at H_2O_2 3%, 98% at H_2O_2 12%.

Figure 3 shows the effects of stirring and H_2O_2 concentration on the total PCDD/PCDFs and the TEQ

reduction. In the case of the total PCDD/PCDFs concentration, there was little difference of results between with stirring and without stirring. In the case of the total PCDD/PCDFs concentration, results are almost the same with those in Figure 1. In the case of the TEQ values, it decreased only a little at H_2O_2 0%. However, it decreased as H_2O_2 concentration increased. At the same H_2O_2 concentration, stirring reduced the TEQ values more. Stirring at H_2O_2 12%, it decreased by 98%.

Results of the Surrounding Soil of a Municipal Solid Waste Incinerator

Figure 4 shows the effects of H_2O_2 percentage on the total PCDD/PCDFs concentration and the TEQ. The total concentration as well as the TEQ decreased as H_2O_2 concentration increased. To be specific, the total concentration reduced by 71% at 3% H_2O_2, and by 84% at 12% H_2O_2. The TEQ reduced by 70% at 3%

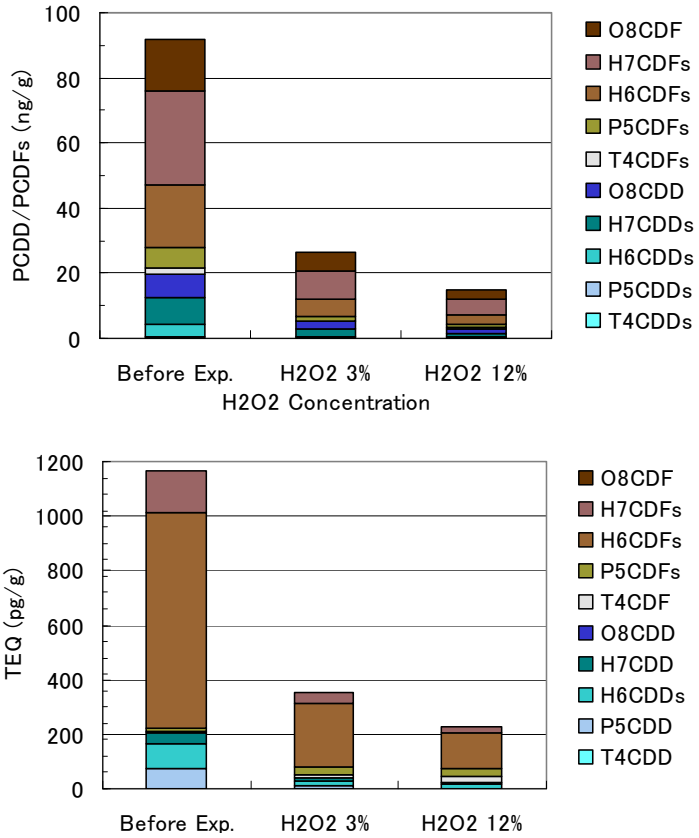

Figure 4. Effects of H_2O_2 concentration (above: Total Dioxin, below: TEQ).

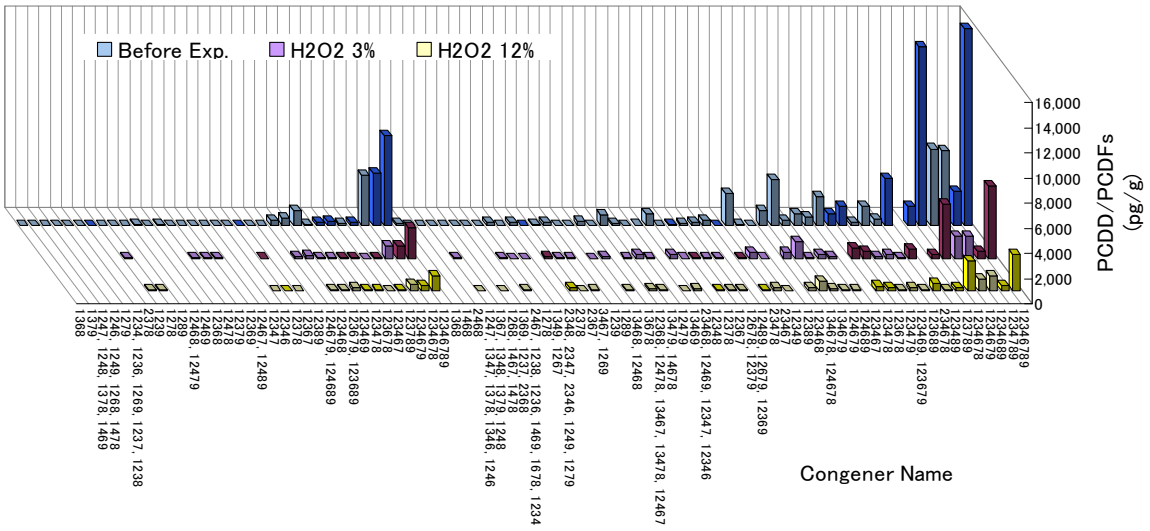

Figure 5. Effects of H_2O_2 Concentration on Congener patterns

H_2O_2, and by 81% at 12% H_2O_2. By using sunlight and H_2O_2 solution, the TEQ was reduced below Japanese Environmental Criteria for Soil (1,000pg/g). Moreover, at 12 % H_2O_2, it reduced below 250pgTEQ/g at which the Japanese administration has to start investigation on dioxin pollution.

Figure 5 shows the effects of H_2O_2 concentration on congener patterns. In the soil sampled at the surroundings of the municipal solid waste incinerator, 133 congeners of PCDD/PCDFs including 17 ones which have TEF were detected. As a consequence of the experiments, a large number of congeners decreased. Congeners with large TEF also reduced. These resulted in the decrease of the total PCDD/PCDFs concentration and the TEQ.

Acknowledgements

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