PHOTODECOMPOSITION OF DIOXIN IN ASH AND PADDY FIELD SOIL

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Abstract

In the Japanese environment, polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and dioxin-like PCBs (Co-PCBs) have accumulated mainly in paddy field soil where the herbicides pentachlorophenol (PCP) and chloronitrophen (CNP) have been applied. The dioxins had been contained in the herbicides unintentionally as byproducts. In this study, a slurry of paddy-field soil or incinerator ash was irradiated using a xenon or mercury lamp with or without hydrogen peroxide (H_2O_2), and the reduction in dioxin concentration and toxicity equivalent quantity (TEQ) values was measured. It was found that the TEQ values of dioxins in 0.3% soil slurry decreased by 95% after Xenon lamp irradiation in the presence of H_2O_2. Generally, higher-chlorinated congeners are decomposed by exposure to irradiation whereas, lower-chlorinated congeners are decomposed to a greater extent by exposure to irradiation in the presence of H_2O_2 .

Introduction

The quantity of dioxins produced during combustion and released as exhaust into the environment has decreased in Japan every year, particularly after the enforcement of the Law Concerning Special Measures against Dioxins in 1999. However, a substantial amount of the dioxins produced unintentionally during the production of the herbicides pentachlorophenol (PCP) and chloronitrophen (CNP) persist in paddy fields nationwide in Japan[1)]. Since there is a possibility that the dioxins go to water system from paddy fields and that they accumulate in the food chain, reduction of dioxins is essential.

Some of the measures reported to reduce the dioxins in the soils are heat treatment and biological treatment[2)]. However, these require time and money. It is well known that dioxins are oxidized by UV; however, sunlight does not penetrate into the soil layers. Therefore, in this study, soil slurry was used as a sample, and the effect of lamp irradiation with and without H_2O_2 on the reduction of dioxins was studied.

Materials and Methods

Material

Three samples were used. Two of these samples were paddy field soils collected in Noshiro City in Akita Prefecture in 2000. In one of these samples termed A, O8CDD was predominant, and the other termed B was rich in T4CDD. When these samples were collected, they were air-dried at room temperature and sieved through a 1 mm sieve. The third sample termed C was incinerator ash; it was obtained from the cleansing water of a municipal incinerator in Niigata City in 2000. The ash sample was dried and crushed.

Method

One gram of soil sample or 0.5 g of ash sample was added to 300 mL of water or H_2O_2 solution. This slurry was placed in a quartz glass beaker, mixed mechanically, and exposed to artificial light. Thereafter, the reduction in dioxin content was measured. A xenon arc lamp (Ushio Optical Modulex: SX-UI 501XQ) or a super-high-pressure mercury lamp (Ushio Optical Modulex: SX-UI501HQ) was used. The distance between the quartz glass beaker and the lamp was 1.0 cm. The angular velocity of the mixer was 720 rad/s. Evaporated water was refilled every 9 h. Figure 1 shows a schema of the experimental devices. The experimental conditions of each test are shown in Table 1

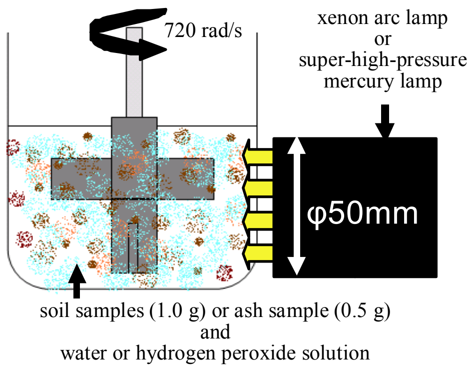

Figure 1 Schema of experimental device

Table 1 Experimental conditions

	Xe-lamp	Xe-lamp + H_2O_2		Hg-lamp + H_2O_2		No light	
Sample	Irradiation time	Irradiation time	H_2O_2 concentration	Irradiation time	H_2O_2 concentration	Stirring time	H_2O_2 concentration
Sample A	0 h 24 h 36 h 48 h 168 h 672 h	36 h	4% 12% 24%			36 h	12%
Sample B	0 h	18 h	12%	18 h	12%		
		36 h	1% 12%	36 h	12%		
Sample C	0 h 36 h	36 h	12%	36 h	12%		

Dioxin Analysis

After irradiation, the samples were filtered through a glass filter paper with a pore size of 1.0 μm. To the filtrate, ^{13}C-labeled internal standards were added. Then, the mixture of the filtrate and the standards was extracted by dichloromethane. On the other hand, the filter paper and the residue on it were extracted by toluene using a Soxhlet apparatus. Each extract was concentrated and the concentrates were then mixed. The mixture was treated with concentrated sulfuric acid and purified by a series of a silica gel column and an active carbon-impregnated silica gel column. The eluate—final PCDD/DF and Co-PCB fractions—were concentrated to 100 μL and spiked with ^{13}C-labeled recovery standards and subjected to high resolution gas chromatography/high resolution mass spectrometry (HRGC-HRMS; Hewlett Packard HP6890/JEOL JMS-700) analysis.

Results and Discussion

Effects of xenon lamp irradiation on dioxin reduction in sample A

Figure 2 shows the relationship between the total concentration of PCDD/DFs and the irradiation time with the xenon lamp. Figure 3 also illustrates the relationship between World Health Organization-toxicity equivalent quantity (WHO-TEQ) values and irradiation time. The concentration of PCDD/DFs decreased with time; however, the reduction in the concentration per hour also decreased with time. With respect to the homologues, the concentration of O8CDD decreased the most with time. O7CDDs exhibited a similar tendency. In the case of TEQ, 1234678-H7CDD decreased with time. In contrast, 2378-T4CDD and 12378-P5CDD increased with time. It is suggested that some of higher chlorinated congeners with lower TEQ values change their form to lower chlorinated congeners with higher TEQ values.

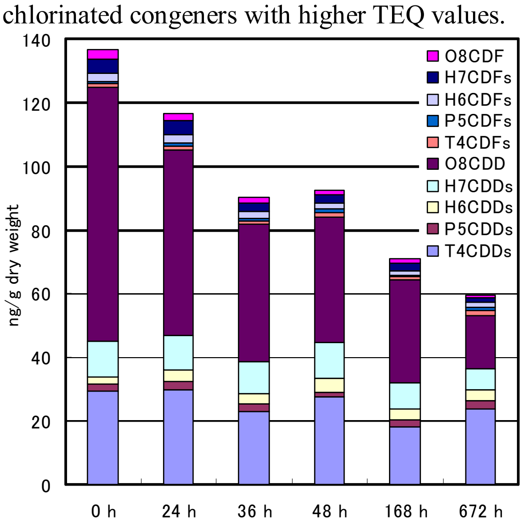

Figure 2
Concentrations of PCDD/DFs after irradiation with the Xe lamp for Sample A

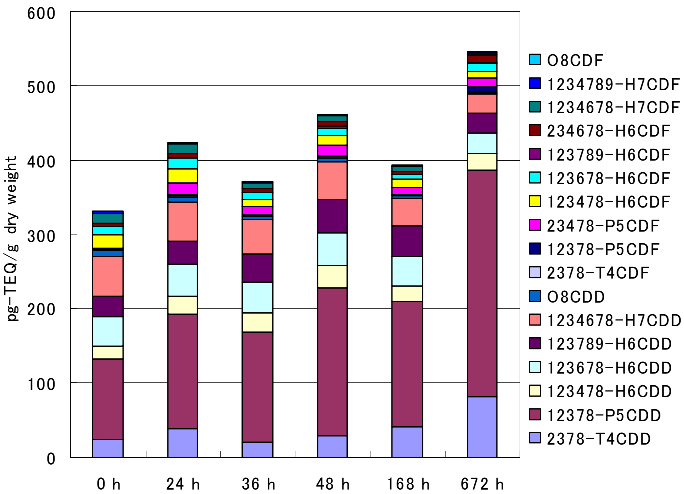

Figure 3
TEQ of PCDD/DFs after irradiation with the Xe lamp for Sample A

Combined effect of Xe lamp irradiation and H_2O_2 on dioxin reduction in sample A

The combined effects of the xenon lamp irradiation plus H_20_2 on the decrease in both total dioxin concentration and TEQ were studied. Figure 4 shows the relationship between the total concentration of PCDD/DFs and H_2O_2 concentration; Figure 5 shows the relationship between WHO-TEQ and H_2O_2 concentration.

The PCDD/PCDF concentrations and the TEQ values were decreased to a greater extent by irradiation in the presence of H_2O_2 (as shown in figures 4 and 5) than by irradiation alone (as shown in figures 2 and 3). In the cases with H_2O_2, the concentration of lower-chlorinated congeners decreased to a greater extent than in the absence of H_2O_2. In addition, the congener with low concentrations of dioxins that barely decreased in the absence of H_2O_2 decreased with H_2O_2. In this experiment, 3 different concentrations of H_2O_2 were used, that is, 4%, 12%, and 24%. A clear relationship between the total dioxin concentration and TEQ concentration and the H_2O_2 concentration was not observed. However, the TEQ reduction rate was high, ranging from 75% to 90%.

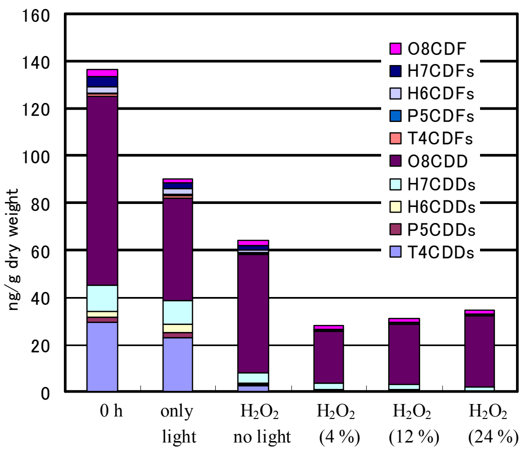

Figure 4
Concentrations of PCDD/DFs after Xe-lamp irradiation combined with H_2O_2 for sample A

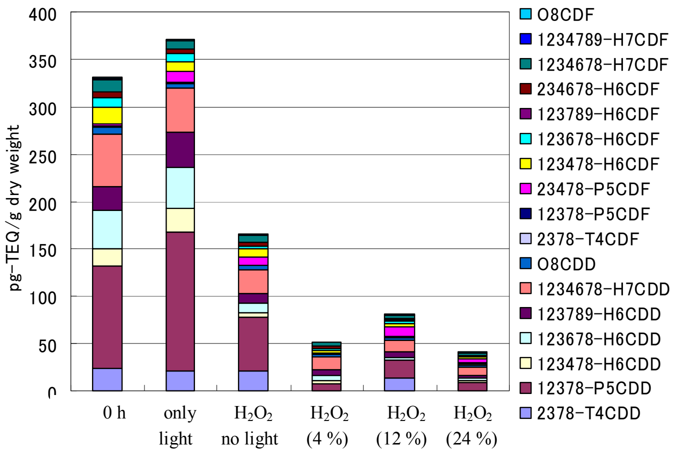

Figure 5
TEQ of PCDD/DFs after Xe-lamp irradiation combined with H_2O_2 for sample A

Effects of irradiation with H_2O_2 on another paddy soil sample B

A different paddy soil sample B, in which T4CDD was predominant, was used to elucidate the effects of a light source, irradiation time, and H_2O_2 concentration. In this experiment, a xenon lamp or mercury lamp was used as a light source; the irradiation time was 18 or 36 h, and the H_2O_2 concentration was 1% only for irradiation with a xenon lamp and 12% for the other cases.

Figure 6 shows the total concentration of PCDD/DFs and Figure 7 shows the TEQ values. Xenon lamp irradiation reduced both total dioxin concentration and TEQ values with time; however, the mercury lamp reduced the only total dioxin concentration with time. After Xe-lamp irradiation for 36-h with 12% H_2O_2, the TEQ values reduced by 95%; however, under the same conditions, the mercury-lamp irradiation reduced the total dioxin concentration by 95%.

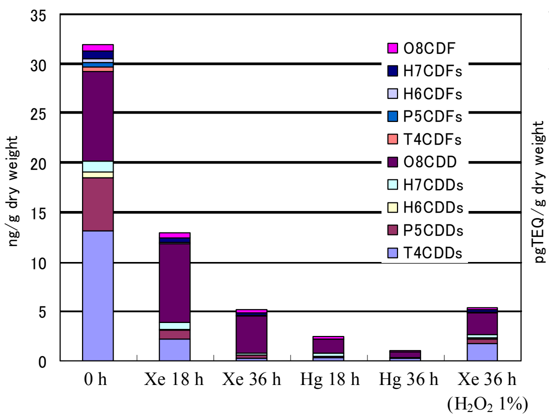

Figure 6
Concentrations of PCDD/DFs after irradiation of sample B

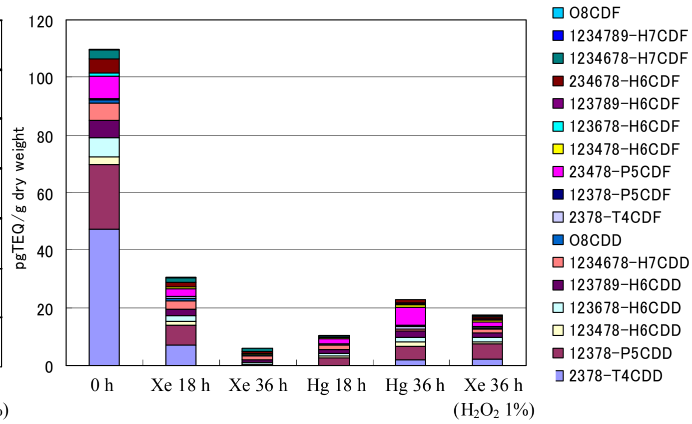

Figure 7
TEQ of PCDD/DFs after irradiation of sample B

Combined effects of irradiation and H_2O_2 on ash sample C

The experimental conditions are shown in Table 1, and the results of the reduction of total dioxin concentration and TEQ values are shown in Figure 8 and Figure 9, respectively. From both the figures, it is evident that a xenon lamp is effective in reducing total dioxin concentration but not TEQ values. However, a mercury lamp is much more effective in reducing both total dioxin concentration and TEQ values. Irradiation by a mercury lamp in the presence of H_2O_2 was found to be very effective in decomposing Co-PCBs.

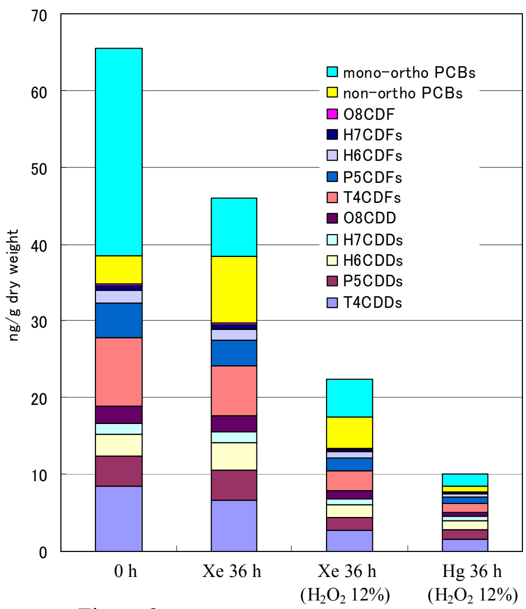

Figure 8
Concentrations of dioxins after irradiation of sample C

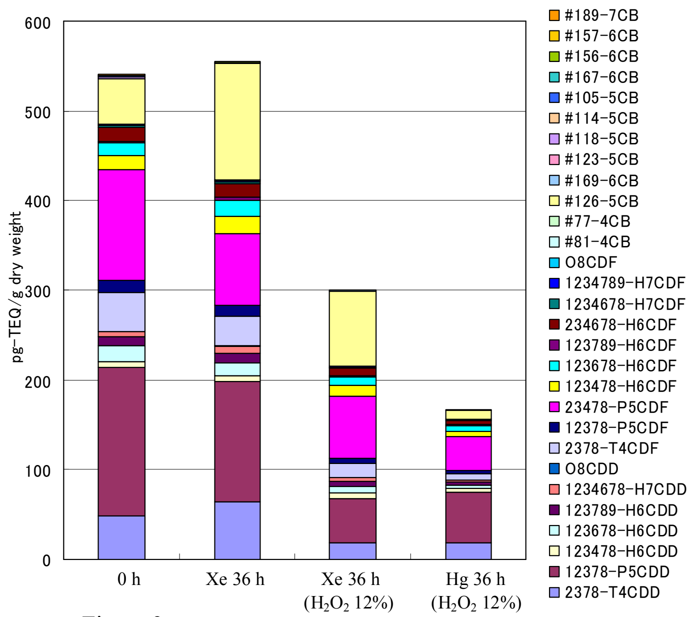

Figure 9
TEQ of dioxins after irradiation of sample C

References

1) Jun Kobayashi, et al.: 12th Symposium on Environmental Chemistry Programs and Abstracts, pp.268–269

2) Mizuki Sakai, et al.: Temporal Trends for Dioxins-related Agrochemicals in Sediments in a Large-Scale Rice-Producing Area, Niigata, Japan, Organohalogen Compounds, vol.66, pp.1475–1478