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Possible Remediation of Dioxin-Polluted Soil by Steam Distillation

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2,7-Dichlorodibenzo-*p*-dioxin (DCDD) was found to evaporate easily with water vapor from a heated solution. Steam distillation was also effective for the removal of DCDD from DCDD-applied soil; its concentration (250 μg/50 g soil) in the original soil decreased to less than 5% after steam distillation for only 20 min. Actual dioxin-polluted soil in Tokorozawa City was partially decontaminated using the same method. These results suggest that steam distillation could be a new remedial method for soils contaminated with persistent environmental pollutants, such as dioxins and polychlorinated biphenyls.

Key words 2,7-dichlorodibenzo-*p*-dioxin; dioxin; detoxification; steam distillation

Dioxins are highly toxic environmental pollutants, mainly generated incidentally in the combustion process of industrial and general waste. In addition to their high toxicity, long-term persistence in the environment is one reason why these pollutants are serious environmental problems.[1] To solve this problem, in addition to the elimination of their generation, it is necessary to degrade and/or detoxify the dioxins that have already accumulated in the environment and will continue to be generated in the future. Several papers have appeared on degradation methods for dioxins.[2—8] However, the ideas or techniques proposed by researchers for the elimination of dioxins do not appear practical, especially in the case of soil pollution. Removal of dioxins should also serve as an effective method for the detoxification of soils, and as a result of removal, some degradation methods might become applicable to the dioxins that have previously been separated from soils.

In the course of our study on the chemical degradation of 2,7-dichlorodibenzo-*p*-dioxin (DCDD) using oxidative reagents, we incidentally found that the added DCDD disappeared rapidly from a heated solution (100 °C) and evaporated with steam. Thus we examined whether steam distillation was useful for remediation of dioxin-polluted soil.

Our preliminary experiments revealed that DCDD disappeared from the heated solution even without oxidative reagents like H_2O_2.[9] Therefore we first examined the evaporation of DCDD from a heated aqueous solution (100 °C). Figure 1 shows the volatility of DCDD from an aqueous solution during steam distillation using an essential oil testing apparatus, together with the data from soil to which DCDD had been applied.[10] Approximately 200 μg of the 250 μg of DCDD applied evaporated from the aqueous solution during the first 10 min, and almost all the remainder was vaporized during the subsequent 10 min. Steam distillation was then applied for the remediation of DCDD-applied model soil. As shown in Fig. 1, the steam distillation of the model soil resulted in almost perfect remediation; the DCDD originally applied was completely recovered in the reservoir of the testing apparatus after 20 min.

Next, we attempted to apply the treatment in the detoxification of the actual dioxin-polluted soil in Tokorozawa City. Table 1 summarizes the analytical results for the dioxin concentration (2,3,7,8-TeCDD toxicity equivalent quantity [TEQ]) in both treated and untreated soils, together with each isomer and congener concentration for polychlorinated dibenzo-*p*-dioxins and dibenzofurans.[11] The original dioxin concentration of 183 pg-TEQ/g decreased to 119 pg-TEQ/g after the treatment. The insufficient removal from the actual polluted soil appeared to be due to a difference in volatility between DCDD and dioxins with more than 4 chlorine atoms: 2,3-DCDD (data for 2,7-DCDD were unavailable), mp 163 °C, saturated vapor pressure 9.3×10^{-3} Pa at 25 °C; 2,3,7,8-TeCDD, 305 °C, 1.2×10^{-4} Pa; and OCDD, 330 °C, 2.8×10^{-7} Pa.[12,13] However, in spite of the large difference in volatility among various isomers, their removal ratios were similar, *ca*. 30% for total TeCDDs and *ca*. 35% for OCDD (Table 1 and Fig. 2). This suggests that the difference in volatility could be ruled out as the reason for the insufficient removal of dioxin from actual soils. However, the existence of evaporable and nonvolatile dioxins in polluted soils may be possible.[14] Even duplicate treatment of the same soils did

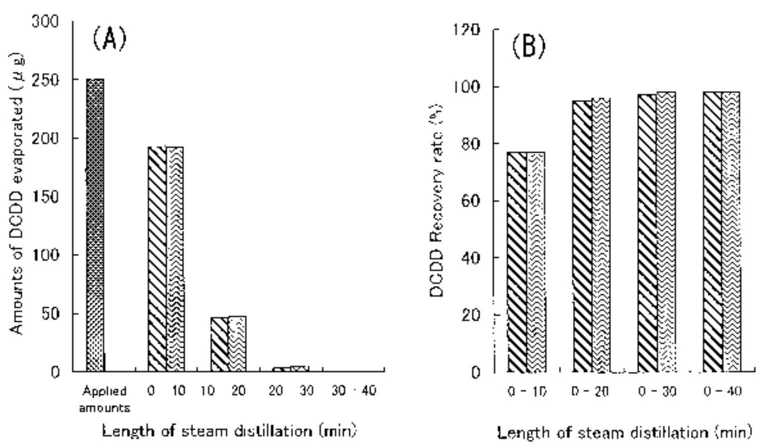

Fig. 1. Volatilization of DCDD from Aqueous Solution and Solution in the Presence of DCDD-Applied Soil During Steam Distillation

(A) Amount of DCDD evaporated. (B) Recovery (%) in the reservoir of the essential oil testing apparatus. ▩, amount of DCDD applied; ▨, water+DCDD; ▧, water+DCDD-applied soil.

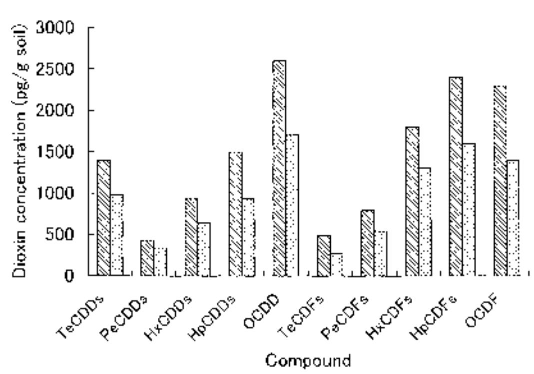

Fig. 2. Comparison of Dioxin Congener Concentration in Polluted Soil (Tokorozawa City) before and after Steam Distillation Treatment

▨, before steam distillation; ▒, after steam distillation.

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Table 1. Results of Analysis of Isomers and Congeners of Dioxins in Polluted Soil (Tokorozawa City) and Soil Treated with Steam Distillation

Compound	Untreated soil		Treated soil	
	pg/g	pg-TEQ/g	pg/g	pg-TEQ/g
PCDDs				
2,3,7,8-TeCDD	1.4	1.4	1.2	1.2
1,2,3,7,8-PeCDD	13	13	9.2	9.2
1,2,3,4,7,8-HxCDD	29	2.9	18	1.8
1,2,3,6,7,8-HxCDD	69	6.9	45	4.5
1,2,3,7,8,9-HxCDD	70	7	48	4.8
1,2,3,4,6,7,8-HpCDD	760	7.6	480	4.8
OCDD	2600	0.26	1700	0.17
Total TeCDDs	1400		980	
Total PeCDDs	430		340	
Total HxCDDs	940		640	
Total HpCDDs	1500		930	
PCDFs				
2,3,7,8-TeCDF	61	6.1	45	4.5
1,2,3,7,8-PeCDF	17	0.85	6.2	0.31
2,3,4,7,8-PeCDF	65	32.5	38	19
1,2,3,4,7,8-HxCDF	280	28	220	22
1,2,3,6,7,8-HxCDF	130	13	79	7.9
2,3,4,6,7,8-HxCDF	470	47	280	28
1,2,3,7,8,9-HxCDF	16	1.6	7	0.7
1,2,3,4,6,7,8-HpCDF	1200	12	820	8.2
1,2,3,4,7,8,9-HpCDF	260	2.6	170	1.7
OCDF	2300	0.23	1400	0.14
Total TeCDFs	490		270	
Total PeCDFs	790		540	
Total HxCDFs	1800		1300	
Total HpCDFs	2400		1600	
PCDDs+PCDFs		182.9		118.9

PCDDs, polychlorodibenzo-*p*-dioxins; PCDFs, polychlorodibenzofurans; TEQ, 2,3,7,8-TeCDD toxicity equivalent quantity.

Table 2. Effects of Plant Ash on Volatilization of DCDD during Steam Distillation

Sample containing DCDD 100 μg	Recovery rate (%)[a]
Water 50 ml	100
Water 50 ml+plant ash 50 mg[b]	67
Water 50 ml+plant ash 500 mg[b]	43
Water 50 ml+plant ash 500 mg[b]+toluene 2 ml	102

a) Removal (%). *b*) It was dried after addition of the AcOEt solution containing DCDD 100 μg.

not improve the removal ratio (data not shown). We speculate that the dioxins in the Tokorozawa City soils probably came from ash generated in an incinerator. It is possible that the ash contained a small amount of carbons, which can adsorb hydrophobic substances such as dioxins. To confirm that carbons inhibit evaporation of dioxins during steam distillation, the effects of carbon-containing plant ash on the evaporation of DCDD were examined. As shown in Table 2, the recovery (ratio of amount evaporated per DCDD 100 μg) decreased with the amount of plant ash. Also of interest is the fact that the low recovery rate (43%) in the presence of plant ash was improved remarkably (by 102%) with the addition of toluene, a solvent used for dioxin extraction.[15] Thus it is possible that polluted soils contain both evaporable dioxins (free dioxins) that are more dangerous to humans and nonvolatile dioxins adsorbed on the surface of carbon particles or organic substances. Steam distillation appears to be a useful method to remove evaporable dioxins from soils.

In summary, DCDD vaporized easily when it was heated with water and was completely removed from the model soil by steam distillation. DCDD is sometimes used in dioxin-related experiments because of its low toxicity. Steam distillation treatment should be effective in removing DCDD from the waste fluid in such experiments. However, steam distillation was insufficient to decontaminate actual polluted soil, with dioxin removal ratios of 30—40%. The remaining dioxins were not removed, even with repeated steam distillation, probably because the adsorptive substances for dioxins, *e.g.*, carbon particles and organic substances, exist in the soils.[14] Nevertheless, steam distillation might be a useful remediation method for dioxin-polluted soils because it can remove the evaporable dioxins that harm humans significantly.

Finally, these results suggest that steam distillation could be a new remedial method for soils contaminated with persistent environmental pollutants such as dioxins and polychlorinated biphenyls.[16] The results also indicate that dioxins other than DCDD vaporize when heated with water. More attention should thus be paid to handling contaminated waste or soils to avoid inhalation of dioxin vapor.

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9) Determination of DCDD was performed with gas chromatography using the capillary column TC-1 (GL Sciences) and a flame ionization detector.
10) "The Japanese Pharmacopoeia 13th Edition," The Ministry of Health and Welfare of Japan, Tokyo, 1996, p. 49. Steam distillation of various samples was carried out by heating the sample and 50 ml of water in a 200-ml eggplant-type flask using an essential oil testing apparatus. To avoid return of the distilled solution to the original flask, a lower valve of the testing apparatus was periodically opened to recover (pool) the water in an Erlenmyer flask. In the place of the xylene used for essential oil testing, 10 ml of AcOEt or hexane was used as a solvent for DCDD or other dioxins, respectively.
11) Analysis of dioxins in the actual polluted soil from Tokorozawa City (Saitama prefecture, Japan) was performed at the Environmental Research Institute Inc. (Maxxam).
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15) An investigation is now under way to determine the effects of various solvents on dioxin recovery in actual dioxin-polluted soil.
16) Steam distillation treatment for polluted soil requires strict attention to avoid dioxin vapor leakage from the apparatus.