

FORMATION AND BEHAVIOR OF POLYCHLORINATED DIBENZOFURANS IN INDIRECT HEATING TREATMENT OF DIOXINS-CONTAMINATED SEDIMENT

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Introduction

Indirect heating treatment (IHT) for dioxin degradation is of promise as a remediation technology, where contaminated soil is cleaned up by dioxins desorption and/or degradation. In Japan, the safety and feasibility in terms of dioxin removals from contaminated soil has been investigated mainly by Ministry of the Environment. However, only a few cases have been applied for contaminated sediment hitherto.

Our previous lab-scale study on screening tests of dioxins-contaminated soil and sediment has revealed that polychlorinated dibenzofurans (PCDFs) generation as by-products is likely to occur in the range of indirect heating temperature from 450 to 600°C. This propensity is amplified when the treatment temperature gets lower. This result is indeed supported by the works by Buser and Rappe, where PCDFs generation is confirmed during thermal degradation at a temperature of lower than 650°C^{1,2}. However, mechanism of dioxin degradation and PCDFs generation by IHT remains still unclear. Therefore, this study investigated reaction pathway from PCBs to PCDFs by IHT. In the experiment, ¹³C₁₂-PCB was spiked to a real sediment sample in order to track the reaction pathway of PCDFs production by HRGC/MS analysis.

Materials and Methods

Figure 1 shows the schematic diagram of the IHT reactor. A sediment sample with ¹³C₁₂-PCB to be treated was mounted on a quartz boat in a quartz tube reactor with an outer diameter and length of 5 and 100 cm. Indirect heating in a furnace was initiated without the sample until heating up to 450°C and subsequently the quartz boat with the sample was slid to the furnace. The heating time was 5 min at temperature of 450°C under 10% O₂/N₂-flow of 1000 ml/min. After the IHT, polychlorinated dibenzo-*p*-dioxins (PCDD)/Fs and polychlorinated biphenyls (PCBs) remaining in the sample and those collected from the quartz tube reactor and the cold/XAD resin/toluene traps, set in the downstream of the IHT reactor, were analyzed. For the analysis, the PCDD/Fs and PCBs were extracted with organic solvent and quantified by HRGC/MS (JSM-700, Tokyo Japan) method in conformity with “the manual of measurement and analysis for soil polluted by dioxins” published by the Environment Agency of Japan (2000). The sample, i.e. sediment contaminated with PCDD/Fs and PCBs (120 pg-TEQ/g), was taken from Tagonoura Bay, Shizuoka in Japan. Stable isotope ¹³C₁₂-PCBs (3,3',4,4'-PCB (#77) and 2,2',4,4',6,6'-PCB (#155)), procured from Cambridge Isotope Laboratories Inc. (Andover, MA), was added to ensure the sample concentration of approximately 10 µg/g. Three runs were performed where no ¹³C₁₂-PCB

(Run 1), $^{13}\text{C}_{12}$ -PCB (#77) (Run 2) and $^{13}\text{C}_{12}$ -PCB (#155) (Run 3) were added in the sediment sample.

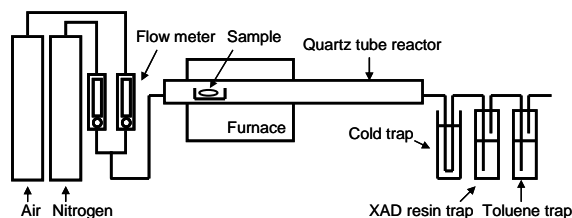


Figure 1 Schematic diagram of the indirect heating treatment (IHT) reactor.

Results and Discussion

(1) Without $^{13}\text{C}_{12}$ -PCB (Run 1)

Figure 2 shows the distributions of PCBs and PCDD/Fs isomers of the original sample. Clearly, the sample contained PCBs with the main component of T3CBs (Panel A) and PCDD/Fs with that of OCDDs (Panel B). In contrast, indirect heating largely produced T4CDFs in the emitted gas as a prominent by-product (Panel B).

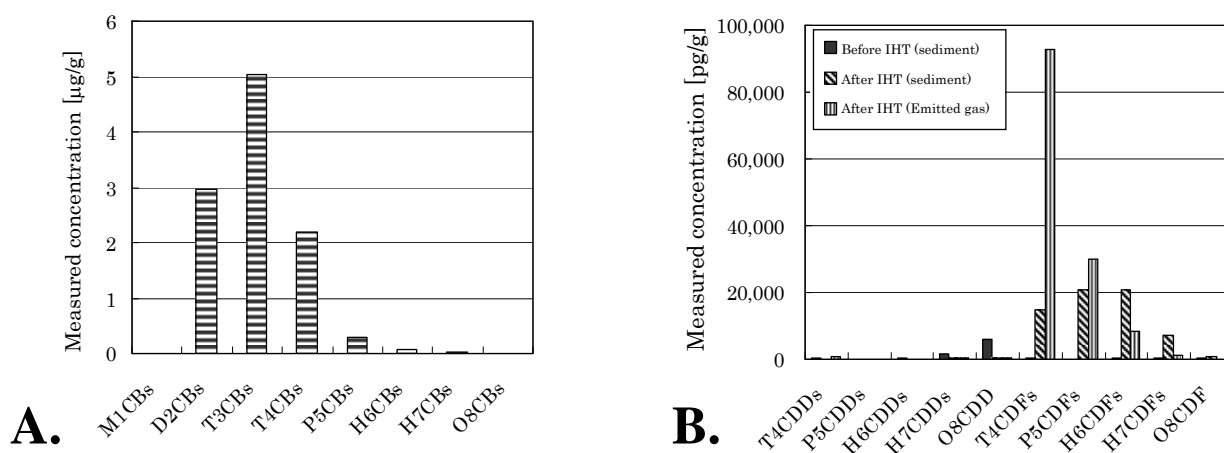


Figure 2 Distributions of PCB (A) and PCDD/Fs (B) isomers in the Tagonoura sediment sample.

(2) With $^{13}\text{C}_{12}$ -PCB #77 (Run 2) and $^{13}\text{C}_{12}$ -PCB #155 (Run 3)

The detection of $^{13}\text{C}_{12}$ -PCDFs indicates T4CDFs in the emitted gas in Run 2 and T4CDFs and P5CDFs in the emitted gas in Run 3 (**Table 1**). The result reveals that part of the PCDFs produced in Run 1 was derived from PCBs as precursors contained in the sediment before the IHT. The chromatogram of $^{13}\text{C}_{12}$ T4CDFs in Run 2 is shown in **Figure 3** as an example. The identification of each peak indicates that the specific $^{13}\text{C}_{12}$ -PCDFs were produced from the added $^{13}\text{C}_{12}$ -PCB in the sediment sample, suggesting that by-product reaction of PCDFs through IHT was likely to occur according to a definite rule, as is proposed by Buser and Rappe^{1,2}. They have

reported that several species of PCBs isomers, each of which was mounted into each glass ampule filled with oxygen and heated at 550-850°C to determine the PCDFs production, have four reaction pathways from PCBs to PCDFs. Furthermore, Groce et al.⁴ have newly found two reaction pathways by using the similar experiment to the one by Buser and Rappe^{1,2}. In total, the six PCBs removal pathways are listed in **Table 2**.

Table 1 Distribution of PCBs isomers in the Tagonoura sediment sample.

	Run 2		Run 3	
	After IHT (Sediment)	After IHT (Emitted gas)	After IHT (Sediment)	After IHT (Emitted gas)
T4CDFs	-	○	-	○
P5CDFs	-	-	-	○
H6CDFs	-	-	-	-
H7CDFs	-	-	-	-
OCDF	-	-	-	-

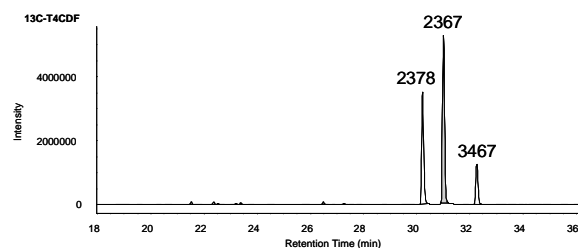


Figure 3 An example of a chromatograph for ¹³C₁₂-T4CDFs in Run 2.

Table 2 Putative removal pathways from PCBs to PCDFs.

Putative removal pathway	Reference(s)
(i) Cl ₂ desorption at ortho position	1, 2
(ii) HCl desorption at ortho position	1, 2
(iii) HCl desorption concomitant with Cl transition from 2 to 3 position	1, 2
(iv) H ₂ desorption at ortho position	1, 2
(v) H ₂ desorption concomitant with Cl transition from 2 to 3 position	4
(vi) H ₂ desorption concomitant with two Cl atoms transition from 2 to 3 and 2' to 3' positions	4

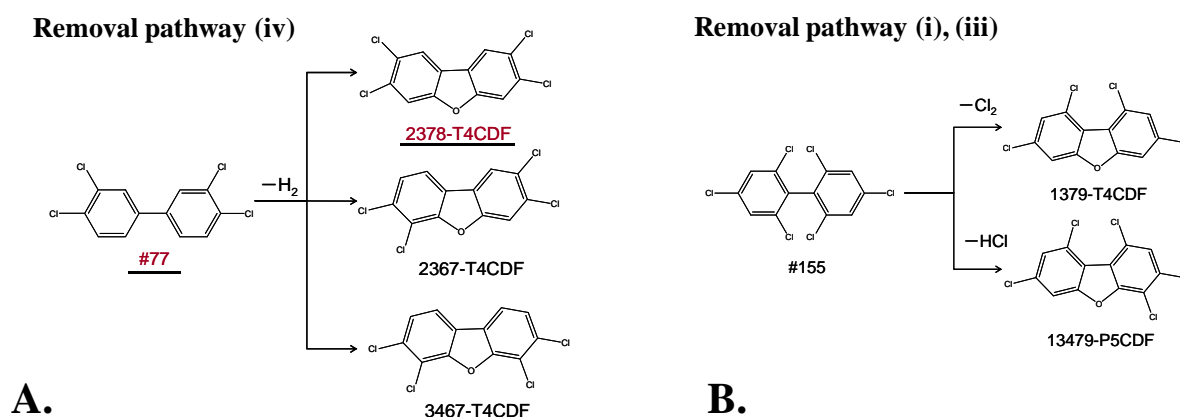


Figure 4 Putative removal pathways from: (A) PCBs (#77) to T4CDF; and (B) PCBs (#155) to T4CDF. The underscored compounds represent toxic isomers.

Conceivable pathways from $^{13}\text{C}_{12}$ -PCBs added in the sediment sample to $^{13}\text{C}_{12}$ -PCDFs detected after the IHT in this study are illustrated in **Figure 4**. The pathways shown in **Figure 4** match the ones previously reported^{1,2}: PCBs #77 (tetrachlorobiphenyl)-added sediment (Run 2) followed the removal pathway (iv) while PCBs #155 (hexachlorobiphenyl)-added sediment (Run 3) did the pathways (i) and (iii) as shown in **Table 2**. Hence, PCDFs by-products production after the IHT of dioxins-contaminated sediment probably stems from the same reaction mechanism with the PCBs thermal treatments previously reported by Buser and Rappe^{1,2} and Groce and Alley⁴.

Conclusion

This study reveals that IHT converts $^{13}\text{C}_{12}$ -PCBs into $^{13}\text{C}_{12}$ -PCDFs through desorption of chloride, hydrochloric acid and hydrogen. These by-product production pathways agree with the one previously proposed by Buser and Rappe^{1,2} and Groce and Alley⁴. Therefore, this indicates that treatment of dioxin-contaminated soil and sediments, containing high concentrations of PCBs, needs to be fastidious especially at 450°C since the condition potentially produces PCDFs, some of which are more toxic than PCBs.

Acknowledgement

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References

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