

PCDDs and PCDFs in Open Ocean Sediment

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1. Introduction

Recently, especially last decade, concentrations of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in various kinds of samples (e.g., waste water, pesticide, sludge, food, industrial material, organism, air and etc.) have been reported by many researchers. Although a few works ^{1), 2) and 3)} which reported the concentrations in coastal and lake sediments are available for us, there has been no report in regard to the open ocean sediment because of their low concentrations and less sampling chance. In the sea floor of open ocean, mass accumulation rate is slow and not disturbed by physical water movement as tide, wave and etc., that the input of the polluted material on the land is limited. Therefore we are easily to get many an information, e.g., background level, historical pollution and geochemical event, through the determination of the concentrations of PCDDs and PCDFs in oceanic sediments.

The purpose of this study is to investigate that detection of PCDDs and PCDFs in oceanic sediment is "possible or impossible".

2. Sample collection

Sediment sample was collected during the TO-91-20 cruise of the research vessel "Tokaidaikumaru-II" belonging to Tokai University. Location of sampling station is listed in Table 1. The sediment sample was collected using a "Box core sampler". This core sampler is available to obtain a non-disturbed sediment core from the deep ocean floor. We collected an 24 cm length core sample from the bottom of 4030m depth. The sediment core was cut every 2 cm thickness after carrying back to the laboratory. PCDDs and PCDFs in a surface sample (0-2 cm) were analyzed by following procedure.

3. Analytical procedure

Extraction

Sediment sample was ground down to fine particle after drying at 25 °C in an auto

drying desiccator. About 200 g (dry weight) ground sample was accurately weighted and put into the pre-washed (toluene and methanol) thimble filter. Sample was spiked with the following Cambridge Isotope Laboratories' $^{13}\text{C}_{12}$ -labeled internal standards; 2,3,7,8-TetraCDD, 1,2,3,7,8-PentaCDD, 1,2,3,6,7,8-HexaCDD, 1,2,3,4,6,7,8-HeptaCDD, 1,2,3,4,6,7,8,9-OctaCDD, 2,3,7,8-TetraCDF, 1,2,3,7,8-PentaCDF, 1,2,3,4,7,8-HexaCDF, 1,2,3,4,6,7,8-HeptaCDF and 1,2,3,4,6,7,8,9-OctaCDF (1 ng of each isomer). Sample was extracted in a Soxhlet extractor using 200 ml methanol and 200 ml toluene for 24 hours respectively. Methanol and toluene were combined after the Soxhlet extractions, and concentrated to 5 ml using rotary evaporator. Then solvent was changed to 100 ml n-hexane.

Clean up

Concentrated sulfuric acid (10 ml) was spiked into n-hexane solution to remove the organic impurities. The treatment of sulfuric acid was carried out three times. N-hexane solution was washed by saturated sodium chloride solution to remove sulfuric acid, then concentrated to 5 ml using rotary evaporator.

The chromatograph technique of silica-gel and aluminum were employed to separate the PCDDs and PCDFs from other impurities in sample. Descriptions for chromatographic technique are omitted here. Final eluent was concentrated using rotary evaporator and solvent was change to toluene.

Finally, toluene solutions were evaporated gently with purified nitrogen gas flow, and concentrated to 100 μl . Toluene final volumes were accurately determined by density of sample solution.

GC/MS determination

The final analysis of PCDDs and PCDFs in extracted sample was performed on high resolution gas chromatograph / high resolution tri-sector mass spectrometer operating in the electron ionization procedure. In order to gain the high resolution and high sensitivity, MS measurements were carried out in one injection for each congener (five injections for one sample). The details of GC/MS conditions are shown in Table 2. Seventeen standards (2,3,7,8-TetraCDD, 1,2,3,7,8-PentaCDD, 1,2,3,4,7,8-HexaCDD, 1,2,3,6,7,8-HexaCDD, 1,2,3,7,8,9-HexaCDD, 1,2,3,4,6,7,8-HeptaCDD, 1,2,3,4,6,7,8,9-OctaCDD, 2,3,7,8-TetraCDF, 1,2,3,7,8-PentaCDF, 2,3,4,7,8-PentaCDF, 1,2,3,4,7,8-HeptaCDF, 1,2,3,6,7,8-HeptaCDF, 1,2,3,7,8,9-HeptaCDF, 2,3,4,6,7,8-HeptaCDF, 1,2,3,4,6,7,8-HeptaCDF, 1,2,3,4,7,8,9-HeptaCDF and 1,2,3,4,6,7,8,9-OctaCDF) were used for determination of each isomer's concentrations.

Clean room

All sample handling and analyses were performed in the "Chemical hazard clean room". The air supplied into this room is passed through several pre-filters and charcoal-filters.

4. Results

In this paper, we report the concentrations of PCDDs and PCDFs in a surface (0-2 cm)

sediment sample. The concentrations of Tetra-, Penta-, Hexa-, Hepta- and Octa PCDD(s) and PCDF(s) are presented in Table 3. The results obtained show that the concentrations of PCDDs and PCDFs in these sample types are very low.

Almost isomers of Penta, Hexa, Hepta and Octa PCDD(s) and PCDF(s) were detected in sample. Some isomers of Tetra CDDs and CDFs were below in the detection level defined as five times the noise (Table 4).

This study suggests that it is possible to detect PCDDs and PCDFs in open ocean sediment. However the analyses require careful pre-concentrations, high resolution and high sensitivity of mass spectrometer.

Table 1. Information of sampling location.

Station Name	Latitude	Longitude	Water Depth	Sampling Date
NT-5(c)	33° 36.9 N	137° 54.9 E	4030 m	Nov., 3rd, 1991

Table 2. Conditions of high resolution gas chromatograph / high resolution mass spectrometer for determination of Tetra-, Penta-, Hexa-, Hepta- and Octa-CDD(s) and CDF(s).

Gas Chromatograph : 5890-SERIES-II (Hewlett Packard)
 Injection Port Temperature : 250°C [for Tetra~Hexa] ; 280°C [for Hepta and Octa]
 Injection Method : 1min. ; splitless
 Injection Volume : 1.0 or 2.0 μ l (using auto injection system)
 Column Head Pressure : 30psi [for Tetra~Hexa] ; 20psi [for Hepta and Octa]
 Carrier Gas : Helium (using gas clean system (GL Science and Superco))
 Rump of Oven Temperature :
 130°C(1min.)--(20°C/min.)-->200°C(0min.)--(3°C/min.)-->250°C(hold) [for Tetra~Hexa] ;
 130°C(1min.)--(20°C/min.)-->220°C(0min.)--(5°C/min.)-->280°C(hold) [for Hepta and Octa]
 Column : SP-2331 fused silica capillary column (Superco)
 60m Length ; 0.25mm ϕ I.D. ; 0.20 μ m Film Thickness [for Tetra~Hexa]
 DB-5 fused silica capillary column (J&W)
 30m Length ; 0.25mm ϕ I.D. ; 0.25 μ m Film Thickness [for Hepta and Octa]

Mass Spectrometer : AutoSpec (VG Analytical)

Detection Method : selected ion monitoring
 Interface Temperature : 250°C [for Tetra~Hexa], 285°C [for Hepta and Octa]
 Ion Source Temperature : 250°C [for Tetra~Hexa], 290°C [for Hepta and Octa]
 Trap Current : 500 μ A, Electron Energy : 40eV
 Resolution : 10,000~15,000 dalton (in 10% Valley) ; Accel Volt 8,000~6,000 V
 Measured Mass : listed in below (PFK lock mass procedure)

Injection no.		Measured Mass		
		for CDD(s)	for CDF(s)	for PFK
1	for Tetra	319.8965, 321.8936	303.9016, 305.8987	318.9792
	for ¹³ C ₁₂ -Tetra	331.9368, 333.9338	315.9419, 317.9389	
2	for Penta	355.8546, 357.8517	339.8597, 341.8568	342.9792
	for ¹³ C ₁₂ -Penta	365.8978, 367.8946	351.9000, 353.8970	
3	for Hexa	389.8156, 391.8127	373.8207, 375.8178	392.9761
	for ¹³ C ₁₂ -Hexa	401.8559, 403.8530	385.8610, 387.8580	
4	for Hepta	423.7767, 425.7737	407.7818, 409.7788	430.9729
	for ¹³ C ₁₂ -Hepta	435.8169, 437.8140	419.8220, 421.8191	
5	for Octa	457.7377, 459.7348	441.7428, 443.7398	454.9729
	for ¹³ C ₁₂ -Octa	469.7780, 471.7750	453.7830, 455.7801	

Table 3. Concentrations of congener for each PCDD(s) and PCDF(s) in a surface sediment sample (0-2cm).

Congeners	Concentration of PCDD(s)	Concentration of PCDF(s)
	(pg/g)	(pg/g)
Tetra	1.6	14
Penta	5.1	7.3
Hexa	19	8.8
Hepta	39	33
Octa	42	20

Table 4. Concentration of each isomer for TetraCDDs and CDFs in a surface sediment sample (0-2cm).

TetraCDDs		TetraCDFs	
Isomers	Conc. (pg/g)	Isomers	Conc. (pg/g)
1,3,6,8-	0.69	1,3,6,8-	0.25
1,3,7,9-	0.52	1,3,7,8-/1,3,7,9-	0.68
1,3,7,8-	0.23	1,3,4,7-	0.33
1,2,4,7-/1,2,4,8-/1,3,6,9-	0.14	1,4,6,8-	0.19
1,2,6,8-	N.D.	1,2,4,7-/1,3,6,7-	0.44
1,4,7,8-	N.D.	1,3,4,8-	0.19
2,3,7,8-	N.D.	1,2,4,8-/1,3,6,7-	0.10
1,2,3,4-/1,2,4,9-/1,2,3,7-/1,2,3,8-/1,2,4,6-	N.D.	1,2,3,7-/1,2,4,6-/1,2,6,8-/1,3,6,9- /1,4,7,8-	2.0
1,2,2,6-/1,2,7,9-	N.D.	1,2,3,4-/2,3,4,9-	1.9
1,4,6,9-/1,2,7,8-	N.D.	1,2,3,6-/1,2,3,8-/1,4,6,7-/2,4,6,8	0.52
1,2,3,9-	N.D.	1,3,4,9-	0.18
1,2,6,9-	N.D.	1,2,7,8-	0.44
1,2,6,7-	N.D.	1,2,6,7-/1,2,7,9-	1.1
1,2,8,9-	N.D.	1,2,4,9-/1,4,6,9-/2,3,6,8	0.54
		2,4,6,7-	1.2
		1,2,3,9-/2,3,4,7	0.35
		1,2,6,9	0.30
		2,2,7,8-	N.D.
		2,3,4,8-	1.3
		2,3,4,6-	0.75
		2,3,6,7-	0.22
		3,4,6,7-	0.99
		1,2,8,9-	N.D.

N.D. : < about 0.1 pg/g (S/N ratio of peak height < 5)

5. References

- 1) Hashimoto S., T.Wakimoto, and R.Tatsukawa (1990) : PCDDs in the sediments accumulated about 8120 years ago from Japanese coastal areas. *Chemosphere* **21**, 825-835
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