TEMPORAL TRENDS OF PCDDs/DFs IN SOIL OF PADDY FIELDS IN JAPAN

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Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) are persistent and toxic environmental contaminants. Recently, it was known that PCDDs/DFs was contained as impurities in paddy field herbicides such as pentachlorophenol (PCP) and chloronitrophen (CNP) [1]. However, the behavior of PCDDs/DFs in the paddy field, such as runoff, advection, degradation, have not ever been elucidated. The objectives of this study are to investigate the temporal trends of the level and source for PCDDs/DFs existing in paddy fields cited in the drainage basin where a large amount of herbicides was used, and to elucidate the behavior of PCDDs/DFs in the drainage basin.

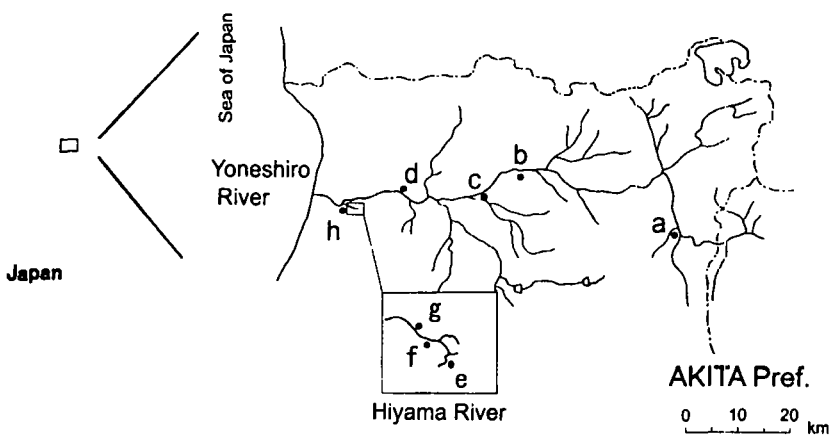

Fig.1 Sampling points in the Yoneshiro River basin

Methods and Materials

Sampling

Soil samples were collected at paddy fields located along the Yoneshiro River basin in 1982, 1984 and 2000. Yoneshiro River runs through paddy field areas in the northern part of Akita Prefecture and discharge into the Sea of Japan. Akita Prefecture is located in Tohoku district and is one of the prefectures in Japan where a large quantity of rice is produced and a large quantity of herbicides for paddy fields are consumed [2]. The number of sampling points is eight, as illustrated in Fig.1. Four sampling points (a, b, c, d) are located along the trunk of Yoneshiro River, three sampling points (e,f,g) are located along Hiyama River, which is branch of Yoneshiro River, and

one point (h) is located near the junction of the two rivers.

Analytical method

Soil samples were collected up to a depth of 5 cm and sufficiently dried at room temperature. Dried samples collected in 1982 and 1984 were preserved in a dark place. Dried samples (10 - 40g) were sieved by a 2 mm mesh sieve. After the addition of 13C-labeled internal standards, each sample was Soxlet-extracted with 300 ml of toluene for 16 hours. Then, they were treated with sulfuric acid oxidation. Sample cleanup included chromatography on silica gel and active carbon-impregnated silica gel. Identification and quantification of PCDDs/DFs homologues were performed by HRGC-HRMS. The separation of PCDDs/DFs was achieved using an HP 6890 instrument equipped with CP-Sil88 and HP-5 columns. TEQ concentrations were calculated based on TEFs for humans revised by the WHO in 1998.

Results

Concentration

Table 1 shows the concentrations of PCDDs/DFs in soil samples collected from paddy fields in the 1980s and 2000. The concentrations of PCDDs were dominant in all sites. The average total concentration of PCDDs/DFs in the soils collected in the 1980s was 88217 pg/g and TEQ was 71.8pg-TEQ/g. In the case of soils collected in 2000, the average total concentration was 88217 pg/g and TEQ was 101.9 pg-TEQ/g. The temporal trend of the concentration for each site was that TEQ concentrations of six sites (a,d,e,f,g,h) increased and those of two sites (b,c) decreased. The sites where the concentrations increased tend to locate in the downstream region.

Table 1. Total and WHO-TEQ concentration of PCDDs/DFs in the soil of paddy fields collected in the 1980s and 2000.

Date of Sampling	Site	Total (pg/g, dry wt.)			WHO-TEQ (pg/g, dry wt.)		
		PCDDs	PCDFs	PCDDs/DFs	PCDDs	PCDFs	PCDDs/DFs
Sep. 1982	a	8794	609	9402	3.5	1.8	5.2
Dec. 1984	b	22882	1006	23888	18.2	2.5	20.6
Nov. 1982	c	160700	4919	165620	66.6	15.5	82.2
Nov. 1982	d	39125	1448	40573	24.8	3.5	28.3
Nov. 1982	e	16594	1205	17798	23.8	4.0	27.7
Nov. 1982	f	114760	2935	117700	79.1	6.9	86.0
Nov. 1982	g	80639	3458	84097	60.3	9.0	69.3
Nov. 1982	h	190350	12878	203230	212.4	42.7	255.1
Average		79230	3557	82789	61.1	10.7	71.8
Nov. 2000	a	11574	561	12135	7.8	1.1	8.9
Nov. 2000	b	16041	619	16660	7.2	1.4	8.6
Nov. 2000	c	73551	1969	75520	31.5	5.7	37.1
Nov. 2000	d	160620	5753	166370	63.7	15.1	78.8
Nov. 2000	e	25729	1299	27028	46.3	10.2	56.5
Nov. 2000	f	82127	7240	89368	173.4	37.5	211.0
Nov. 2000	g	89254	3323	92577	62.6	10.0	72.6
Nov. 2000	h	211860	14227	226080	288.0	53.7	341.6
Average		83845	4374	88217	85.1	16.8	101.9

The concentrations of nine of the 16 samples exceeded the average concentration of 48.1 pg-TEQ/g, which was obtained in the investigation of paddy fields by the Japan Environment Association [3]. The concentrations in the downstream region tended to be higher than those in the upstream region.

Homologue Distribution

The homologue distribution is shown in Fig.2. The characteristic that T4CDDs and T8CDDs were dominant was common for all samples. Eight sites were classified into two groups: Group 1 (sites a, b, c, d, e, g) where the level of T4CDDs was larger than that of O8CDD and Group 2 (sites f, h) where the level of O8CDD was larger than that of T4CDDs. The temporal change was found to be larger for T4CDDs than for O8CDDs for almost all sites.

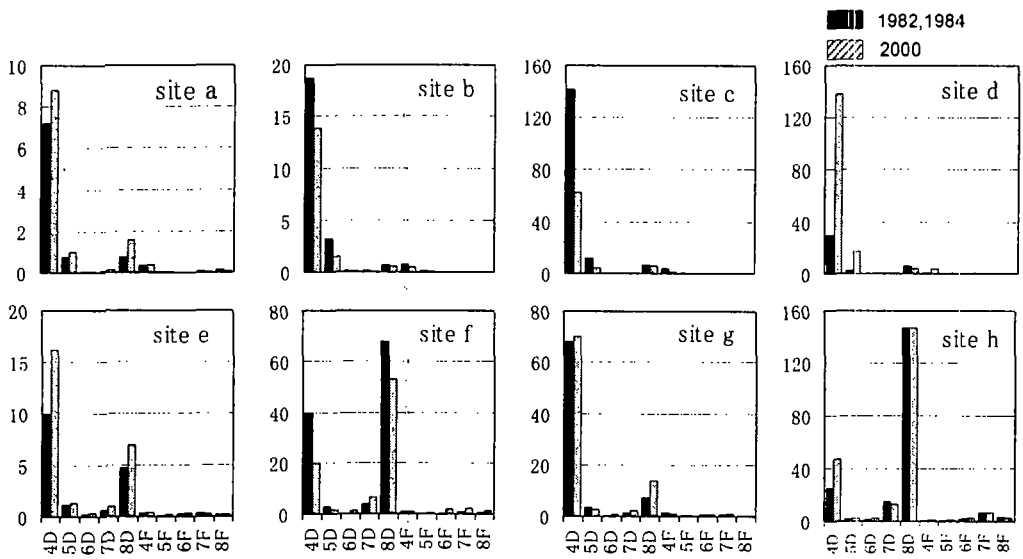

Fig.2 Homologue distributions of PCDDs/DFs of the paddy fields soil (ng/g dry wt.)

Multivariate Analysis

To identify the possible sources of dioxins, principal component analysis (PCA) was applied to congener-specific data (37 GC peaks corresponding to an individual or group of congeners were used as variables and 16 soil samples, as cases). PCA yielded two major principal components (PCs) (Table 2). Based on the characteristic congeners in each PC, PC-1 and PC-2 were judged to be the impurities in CNP and PCP, respectively.

The contribution of the two sources to soil pollution was estimated by multiple regression analysis (MRA) using the congener profiles of PCP and CNP. The congener profile of PCP produced in 1967 [4] and that of CNP produced in 1983 [4] were used for MRA. MRA calculations were performed for each homologue and then the summation was taken [1]. The results of MRA are shown in Fig.3. The temporal change of PCDDs/DFs originating from CNP was marked, however, the change of PCDDs/DFs from PCP was small for all sites.

Discussion

The tendency that concentrations in the downstream region are higher than those in the upstream region seems to be due to the fact that PCDDs/DFs transported by the flow of the river have accumulated in the paddy fields located downstream. The fact that PCDDs/DFs originating from PCP have not fluctuated so much while those originating from CNP have fluctuated seems to be due to two factors. One is the difference in the period when two herbicides had been used. The usage period of PCP is from 1955 to 1974 while that of CNP is from 1965 to 1994. The other factor is the difference in the property of congeners consisting of PCDDs/DFs contained in both herbicides as impurities. The solubility in water of congeners contained in CNP was higher than that of congeners contained in PCP; therefore PCDDs/DFs originating from CNP is more easily transported by river flow than those from PCP.

Table 2 Results of Principal Component Analysis

Principal Component	Proportion (%)	Characteristic congeners (congeners with high factor loading)	Interpretation (Probable source)
PC-1	52	1368,1379-T4CDD 2468-T4CDF	Chloronitrophen (CNP)
PC-2	41	O8CDD, some of H7CDDs/Fs	Pentachlorophenol (PCP)

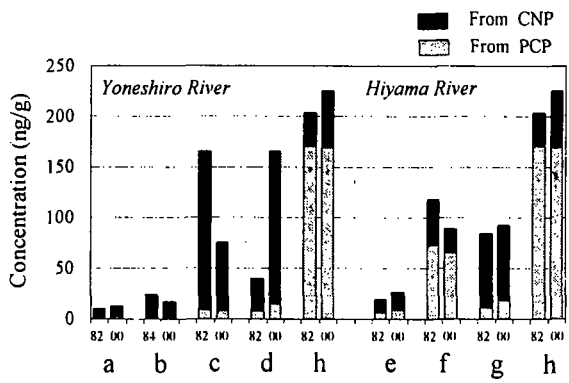

Fig.3 Contributions of two herbicides to dioxin pollution in paddy field soil along Yoneshiro River basin.

Acknowledgements

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