PCDD/Fs Concentration in Paddy Field Soil and Their Outflow to River System

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Abstract

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) were included as impurities of the organochlorine herbicides (ex. CNP: 1,3,6,8-, 1,3,7,9-TeCDD, PCP: OCDD) in Japan[1], and the large amount of them are remaining in paddy soil even in recent years with the concentrations of about 20- 200pg/g. Those PCDD/Fs may flow out from ricepad into adjacent river system with cultivational operations like paddy soil mixing or rice transplanting. Distribution of PCDD/Fs in the soil and in river water were analysed focussing on the behavior of fine soil particles. Estimation of the annual discharge of fine paddy soil indicated that at least some part of reduction of PCDD/Fs concentration in paddy soil is attributed to outflow of paddy soil.

Introduction

Although various studies have been carried out, the main factor of gradual reduction of PCDD/Fs concentration in paddy soil is still not clear. One of possible machanisms is an outflow of soil-bond PCDD/Fs into river system. Japanese Ministry of the Environment carried out an experiment in 2002 in relation to PCDD/Fs redistribution in the environment using a ricepad as a model, and estimated that annual discharge rate is only 0.00083-0.012% (ave. 0.0048%) from ricepad to public river system[2]. However, in field observation, river water often contains a significant amount of suspended materials in plantation season when puddling and transplantation are being done suggesting that discharge rate may be much bigger than the former estimation. In this study, we measured PCDD/Fs concentration in river water in Matsuyama Plain and in soil/sedimental samples as well as suspended particles to estimate annual discharge of paddy soil and PCDD/Fs into receiving river system.

Materials and Methods

Samples of the paddy soils, paddy water, creek and river waters and bottom sediments were collected along Kunichika River and its basin in Matsuyama Plain, Ehime Prefecture. Sampling sites of this study are shown in Fig. 1. and the sampling was conducted from 2002 to 2004.

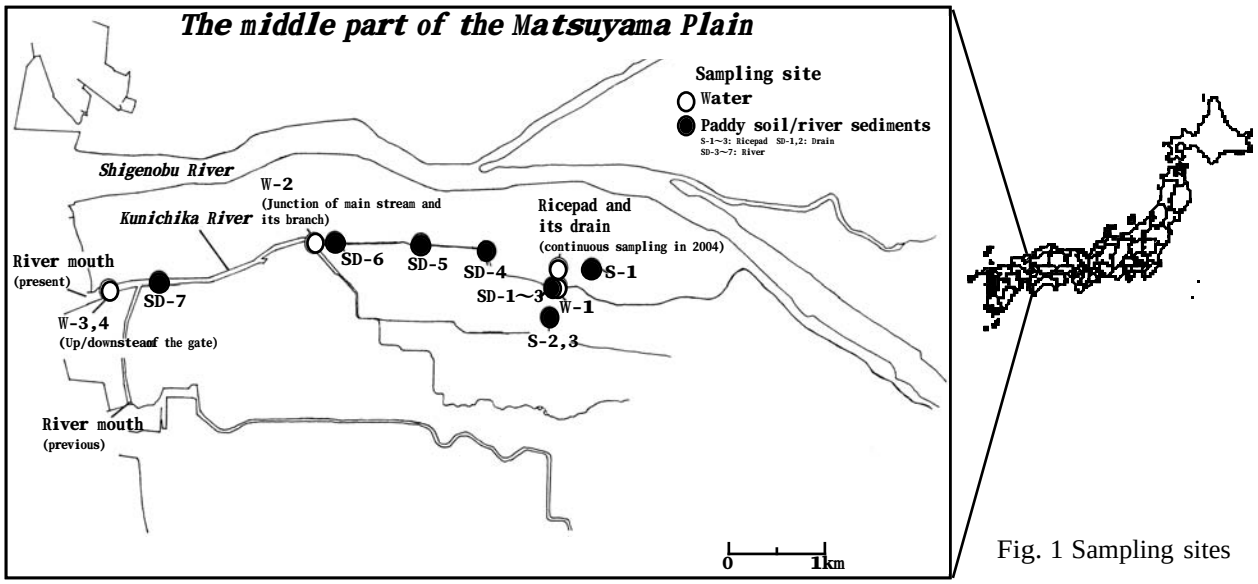

Fig. 1 Sampling sites

We carried out following 3 experiments and analyses.

1. Field sample analyses River water samples were analysed for fine particle concentration and for PCDD/Fs. PCDD/Fs were also analyzed in sediment and paddy soil samples: 50 g of either sediment or paddy soil was used for PCDD/Fs analysis based on the method by Seike et al(2002)[1].

2. Laboratory experiment (1) Soil suspension and characterization of suspended particles in water: 0.1 g of paddy soils or bottom sediments was shaken with 50 ml of water and subjected to particle analysis includingparticle size distribution and particle concentration. (2) PCDD/Fs analysis in suspended and precipitated particles: 10 g of paddy soil was put into glass cylinder together with 2 liters of water. After shaking and left standing for a designed time, suspended material and precipitated material were separated and collected by filtration. Three standing time (30minutes, 2hours and 6hours) were examined for time course effect of sedimentation. PCDD/Fs concentration in suspended and precipitated particles were analyzed according to the method of experiment 1.

3. Monitoring of suspended particle in river water during plantation season. River water was sampled at every two days interval from May to July in 2004 and subjected to analysis of particle number and size distribution.

Results and Discussion

PCDD/Fs concentration in river sediment is shown in Table 1 together with paddy field soil and sediment in the drainage between river and paddy field. Geographical distribution of PCDD/Fs along the river is clear: PCDD/Fs are high at rice plantation area and become low downstream. Analysis of suspended fine particles in the river water also showing similar figure suggesting that the major source of PCDD/Fs in this river is rice plantation field and that fine soil particle carries PCDD/Fs from the field to the river. River water becomes turbid in transplantation season receiving fine particle rich water from rice paddy field.

Table 1 The results of particle and PCDD/Fs analyses.

Soil/sediment	Paddy soil (n=3)	Drainage sediment (n=2)	River sediment				
			SD-3	SD-4	SD-5	SD-6	SD-7
All particle number (/μl)	5005.8	880.6	1669.0	292.5	448.8	136.3	195.0
Mode diameter (μm)	1.56	1.28	1.71	3.83	2.09	1.24	1.66
Mean Diameter (μm)	3.84	6.38	4.42	10.01	6.98	3.75	5.36
ϕ<10μm particle portion (accum. %)	95.4	92.2	94.1	85.9	83.6	95.4	91.2
ϕ<10μm particle number (/μl)	4822.9	810.5	1571.0	251.2	375.1	130.1	177.8
Total PCDD/Fs (pg/g-dry)	50886	8348	6180	8592	6820	2272	728

Figure 2 shows the depth profile of PCDD/Fs in paddy field. Paddy field is contaminated by specific isomers of PCDD/Fs arising from major herbicide applied to the field. 1,3,6,8-TCDD and 1,3,7,9-TCDD come from CNP and OCDD comes from PCP applied more than 30 years ago. Their concentrations are high in the surface and becomes very low below 22 cm depth. It is due to the puddling practice that mixes soil between 0-20 cm depth with stored water. In this practice, fine particles, often silt-clay composition, was stirred up and forms turbid water by suspension.

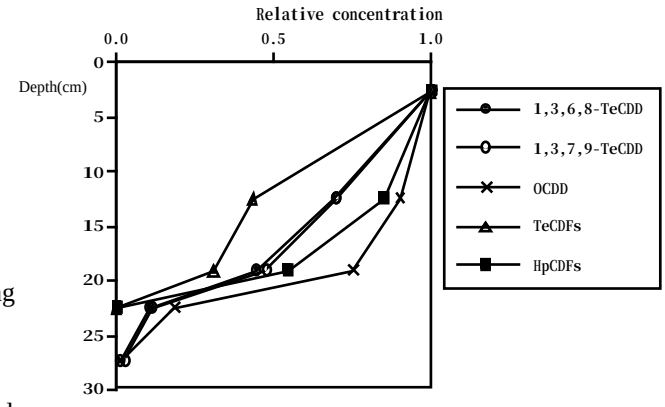

Fig. 2 Vertical profile of PCDD/Fs relative concentration

In the laboratory experiments, we examined the relation between suspended particle concentration and PCDD/Fs concentration using paddy soil and bottom sediments (Table 2).When soil was mixed with high volume of water and left standing for a short time, fine particles remains

in aqueous phase and large size particles precipitate soon.

The result of the experiments shows that particles with small size (ϕ<10μm in diameter) remains aqueous layer as suspended. It was noted that paddy field soil contains more "suspendable" soil than the river sediment downstream. It was also noted that "suspendable" or fine particles contains more PCDD/Fs than the coarse soil or sedimental particles.

Table 2 PCDD/DFs concentration in suspended particle and precipitated particle in paddy soil (pg/g)

(a) The result of experiment 2(a)

Isomer	Suspended particle (n=3)			Precipitated particle (n=3)			Original soil (n=1)
	Min.	Max.	Mean	Min.	Max.	Mean	
1,3,6,8-TeCDD	11000	26000	16000	9300	10000	9700	13000
1,3,7,9-TeCDD	3700	9100	5500	3100	3800	3400	5100
2,3,7,8-TeCDD	ND	ND	ND	ND	ND	ND	ND
1,2,3,7,8,-PeCDD	(40)	ND	(40)	4.6	5.0	4.8	ND
1,2,3,4,7,8-HxCDD	ND	ND	ND	4.2	6.0	4.8	8.5
1,2,3,6,7,8-HxCDD	(11)	(30)	(18)	(8.9)	(9.4)	9.1	12
1,2,3,7,8,9-HxCDD	(9)	(10)	(9.5)	(8.4)	(8.7)	(8.5)	10
1,2,3,4,6,7,8-HxCDD	170	470	270	160	180	170	240
OCDD	1700	6400	3300	2300	2500	2400	2600
1,2,7,8-TeCDF	(5.0)	(20)	(13)	(2.3)	(2.6)	(2.5)	ND
2,3,7,8-TeCDF	(4.0)	(4.0)	(4.0)	1.6	1.9	1.8	2.2
1,2,3,7,8-PeCDF	(3.0)	(10)	(5.7)	ND	ND	ND	ND
2,3,4,7,8-PeCDF	ND	ND	ND	ND	ND	ND	ND
1,2,3,4,7,8-HxCDF	ND	ND	ND	ND	ND	ND	ND
1,2,3,6,7,8-HxCDF	ND	ND	ND	ND	ND	ND	ND
1,2,3,7,8,9-HxCDF	ND	ND	ND	ND	ND	ND	ND
2,3,4,6,7,8-HxCDF	(9.0)	(30)	(20)	(5.6)	(6.1)	(5.8)	6.2
1,2,3,4,6,7,8-HpCDF	ND	ND	ND	14	15	14	17
1,2,3,4,7,8,9-HpCDF	ND	ND	ND	ND	ND	ND	ND
OCDF	ND	ND	ND	15	16	16	17
TeCDDs	15000	35000	22000	3900	14000	10000	18200
PeCDDs	1600	4100	2400	1600	1700	1600	2200
HxCDDs	130	350	210	140	140	140	190
HpCDDs	340	1000	560	330	370	350	490
OCDD	1700	6400	3300	2300	2500	2400	2600
Total PCDDs	19000	47000	29000	8300	18000	14000	24000
TeCDFs	490	1200	740	370	400	390	430
PeCDFs	82	240	130	60	64	62	78
HxCDFs	(10)	(60)	34	30	32	31	42
HpCDFs	ND	ND	ND	30	32	31	38
OCDF	ND	ND	ND	15	16	16	17
Total PCDFs	590	1500	910	490	540	520	600
Total PCDD/Fs	19000	49000	29000	8900	19000	15000	24000
Weight (g)	0.1	0.4	0.3	10	30	20	10

*Separation of suspended and precipitated particle of all samples was carried out within 30 minutes.

(b) The result of precipitaion experiment 2(b)

Situation	Total PCDD/DFs (pg/l)
30 minutes after shaking	9800
2 hours after shaking	3500
6 hours after shaking	2800

If PCDD/Fs are carried by fine particles in the water system, measurement of fine particles in river water is valuable for assessing fate of PCDD/Fs. River water was analysed for the concentration of fine particles during transplantation season. By multiplying measured concentration with water flow rate, we can estimate the volume of delivered soil particle in a day. The result is shown in Fig. 2. There seems a peak discharge of particle in early June. In this season paddy field is fulfilled with water, and then puddled mechanically to mix the soil, and some portion of water is drained off, and finally young rice plants are transplanted by the machine and unnecessary water is to be drained off slowly. The peak inflow of suspended materials into the river is coincides with the discharge of paddy field water. PCDD/Fs in the paddy field may be lost in this process and delivered to river and coastal area.

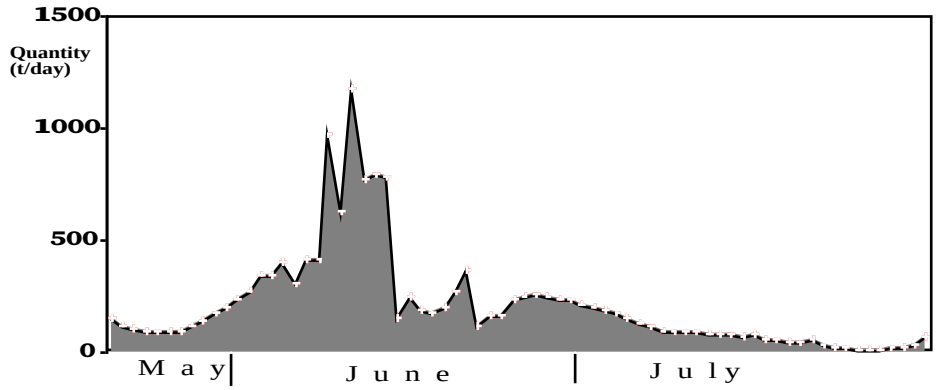

Fig. 3 Calculated discharge amount of suspended particles at W-2. Continuous sampling was carried out in 2004.

OCDD concentration in the paddy soil in Matsuyama Plain is reported decreasing slowly. A part of the reduction may be attributed to the outflow of the paddy soil.

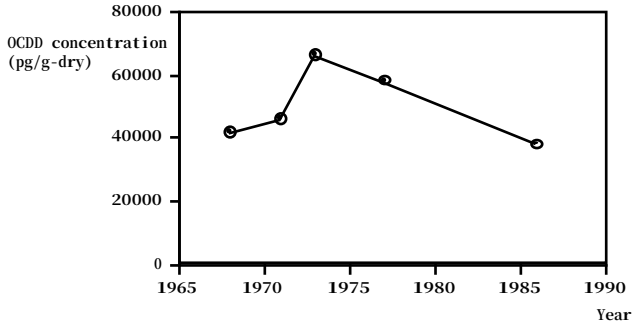

Fig. 4 Time trend of OCDD in paddy soil, Matsuyama Plain[4] (altered)

Acknowledgements

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