Temporal trend and mass balance of POPs in paddy fields in Japan

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Introduction

Most of Persistent organic pollutants (POPs) has been used as agrochemicals in farmlands worldwide,especially, in Japan, where PCDD/DFs had contaminated to paddy fields as impurities in herbicides, pentachlorophenol (PCP) and chloronitrophen (CNP)[1, 2]. However, the behaviour of POPs in the paddy fields have not been elucidated. In this paper, We investigated behaviour of POPs in Japanese paddy soils to make clear their temporal trend, the relationships between each POPs, the mass balance and so forth.

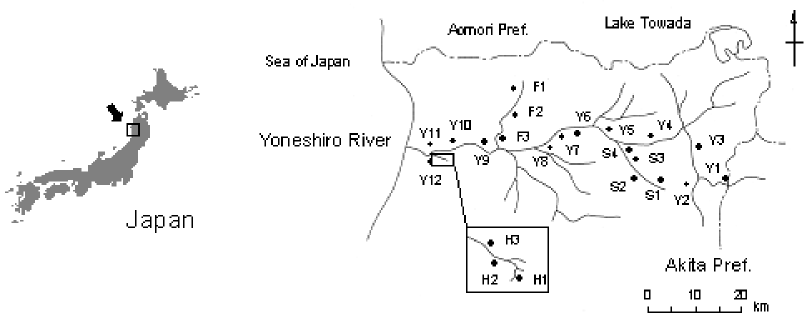

Fig. 1. Sampling points in the Yoneshiro River basin in Akita Perfecture.

Methods and Materials

Study area and sampling

The study area and sampling points were shown Figure 1. The Yoneshiro River runs throuuh paddy fields' areas from the east to the west in the northern part of Akita Prefecture. Samples were taken at 22 points in the river basin both in 1980s (1982, 1984) and in 2000s (2000 and 2002). But some samples collected in the 1980s were not analyzed because of the lack of sample weight. One sample at S4 could not be taken in the 2000s because of the urbanization. More details of the study area and the sampling were refered to the previous report[2].

Target chemicals

The target chemicals for analysis in this study were Aldrin, Dieldrin, Endrin, Chlordanes (*cis-, trans-*),DDTs (*p,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE), Heptachlor, Heptachlorepoxide,HCHs (α-, β,- γ-, δ-), HCB,PCBs and PCDD/DFs. The target chemicals except for PCBs and PCDD/DFs are called organochlorine pesticeds (OCPs) hereafter in this report.

Analysis method

Sample preparation and the analysis method of PCDD/DFs are the same with the previous report[3]. The analysis of OCPs and PCBs were conducted as follows. First, 17-20g ofthe samples were Soxlet-extracted with 300 ml of toluene for 16 hours. Then, the extract was divided into two to analyze PCBs and OCPs. The one half extract for OCPs analysis was cleaned up using Florisil chromatography. Then, the eluate was introducedto a GC/MS (SHIMADZU GC17A/QP5000) equipped with DB5-ms (Agilent). The other half extract for PCBs analysis was cleaned up using sulfuric acid oxidation, silica gel chromatography, and for some samples, active carbon impregnated silica gel chromatography. All 209 congeners of PCBs were measured using a HRGC/HRMS (JEOL HP6890/JMS 700) equipped with DB5 (Agilent).

Results and Discussion

POPs concentrations in the paddy soils

Table 1 shows a summary of the study; the mean, minimum, and maximum concentrations (ng/g dry weight or pg-TEQ/g dry weight) for target chemicals. Aldrin, dieldrin, endrin, chlordanes, heptachlors were scarcely detected from almost all samples collected in the 1980s and 2000s. DDTs, HCHs, HCB, PCBs, PCDD/DFs were detected from most of samples collected in the 1980s and 2000s. As for the average concentrations of the samples collected in the 1980s and 2000s, DDTs were 9.1 ng/g, 2.4 ng/g, HCHs was 63 ng/g, 6.1 ng/g, HCB was 0.46 ng/g, 0.25 ng/g, PCBs was 7.0 ng/g, 1.8 ng/g, PCDD/DFs was 60 pg-TEQ/g, 80 pg-TEQ/g, respectively. Though PCBs and HCB had never been applied as agrochemical to the paddy field in Japan, their concentrations were not so differ from concentrations of other OCPs. The detected POPs except PCDD/DFs in the paddy soil were decreased greatly from the 1980s to 2000s whereas PCDD/DFs were not decreased from the 1980s to 2000s. This result is thought to be due to two reason, the difference of their applied period and their chemical and physical property. POPs except PCDD/DFs had not been applied to the paddy field after the 1970s, whereas PCDD/DFs had been applied as impurities in herbicides (PCP and CNP) to the paddy field until early 1990s[1].

Table 1. The concentrations of POPs in the paddy soils in the 1980s and 2000s.

Sampling year	1982, 1984				2000, 2002			
	Avg.	Min.	Max.	Detections /Samples	Avg.	Min.	Max.	Detections /Samples
Aldrin (ng/g)		N.D. (<0.48)		0 /21		N.D. (<0.48)		0 /21
Dieldrin (ng/g)	0.28	N.D. (<0.54)	5.8	1 /21		N.D. (<0.54)		0 /21
Endrin (ng/g)		N.D. (<0.35)		0 /21		N.D. (<0.35)		0 /21
Chlordanes (ng/g)	1.1	N.D.	23	1 /21		N.D.		0 /21
cis-Chlordane (ng/g)	0.97	N.D. (<0.12)	20	1 /21		N.D. (<0.12)		0 /21
trans-Chlordane (ng/g)	0.12	N.D. (<0.64)	2.4	1 /21		N.D. (<0.64)		0 /21
DDTs (ng/g)	9.1	N.D.	87	19/ 21	2.4	N.D.	7.7	19 /21
p,p'- DDT (ng/g)	0.42	N.D. (<0.59)	4.4	3/ 21	0.28	N.D. (<0.59)	2.4	3 /21
p,p'- DDD (ng/g)	6.6	N.D. (<0.17)	75	18/ 21	0.69	N.D. (<0.17)	2.1	12 /21
p,p'- DDE (ng/g)	2.1	N.D. (<0.38)	9.7	17/ 21	1.4	N.D. (<0.38)	3.3	19 /21
Heptachlors (ng/g)	0.67	N.D.	5.9	3 /21		N.D.		0 /21
Heptachlor (ng/g)	0.67	N.D. (<0.13)	5.9	3 /21		N.D. (<0.13)		0 /21
Heptachlor epoxide (ng/g)		N.D. (<0.25)		3 /21		N.D. (<0.25)		0 /21
HCHs (ng/g)	63	N.D.	380	18 /21	6.1	N.D.	72	10 /21
α-HCH (ng/g)	8.2	N.D. (<0.43)	99	16 /21	1.2	N.D. (<0.43)	9.2	8 /21
β-HCH (ng/g)	47	N.D. (<0.41)	340	18 /21	4.6	N.D. (<0.41)	59	10 /21
γ-HCH (ng/g)	0.095	N.D. (<0.49)	2.0	1 /21		N.D. (<0.49)		0 /21
δ-HCH (ng/g)	7.9	N.D. (<0.92)	51	10 /21	0.36	N.D. (<0.92)	3.5	3 /21
HCB (ng/g)	0.46	N.D. (<0.44)	1.9	9 /21	0.25	N.D. (<0.44)	2	6 /21
PCBs (ng/g)	7	1.6	14	17 /17	1.8	1.0	4.4	21 /21
PCDD/DFs (ng/g)	89	7.2	390	19 /19	84	15	230	21 /21
PCDD/DFs (pg TEQ/g)	60	1.8	230	19 /19	80	3.3	320	21 /21

Persistence

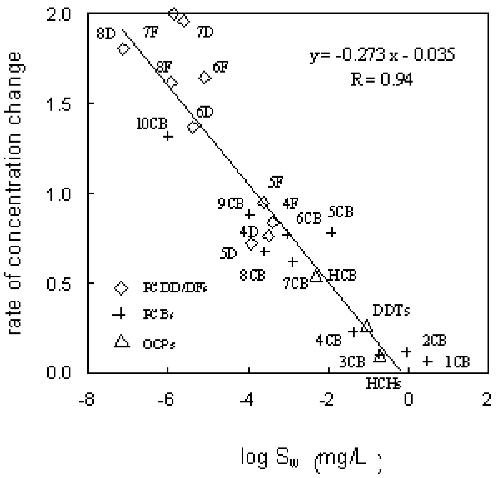

Fig. 2. The relationship between the rate of concentration change and log water solubility.

In order to elucidate persistence of each chemical in the paddy soils, the correlation between the rate of concentration change and chemical and physical properties (the water solubility (S_w), the octanol/water partition coefficient (K_{ow}) and the vapor pressure) were studied, where the rate of concentration change was defined as ratio between theaverage concentration in the soil samples collected in the 2000s to the 1980s. Fig. 2 shows the relationship between the rate of concentration change and log S_w.The rate of concentration change and log S_w were highly correlated (R=0.94).The rate of concentration change also showed high correlation to log K_{ow}orlog vapor pressure, correlation coefficient, R, was 0.81 and 0.88 respectively. It was indicated that out-flow and volatilization largely contribute to disappearance of POPs from the paddy soils.

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Mass balance of DDT and HCH in the Yoneshiro River basin

In order to understand the fate of POPs in the Yoneshiro River basin, we estimated the mass balance of DDT and HCH. The mass balance of DDT was shown in Fig. 3. The amount of input to the river basin from 1962 to1971 was estimated to be 13 ton, whereas the remaining amount at 2002 was estimated 0.092±0.080 ton. The mass balance of HCH is summarized in Fig. 4. The amount of input to the river basin from 1962 to1971 was estimated to be 110 ton, whereas the remaining amount at 2002 was estimated 0.23±0.61 ton. Thus, more than 99% of DDT and HCH amounts applied to the river basin were estimated to be disappeared. On the other hand, in the case of PCDD/DFs, our study made clear that the difference between the estimated amount of input and remaining was small[2]. It is thought that the disappearance processes of POPs observed in this study were mainly caused by out-flow and volatilization, not caused by decomposition, because the rates of concentration change were highly correlated with the log water solubility, the log Kow and the log vapor pressure.

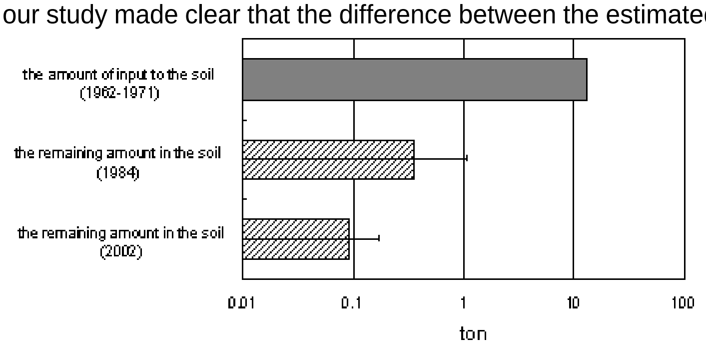

Fig. 3. The estimated the amount of input and remaining of DDT in the Yoneshiro River basin.

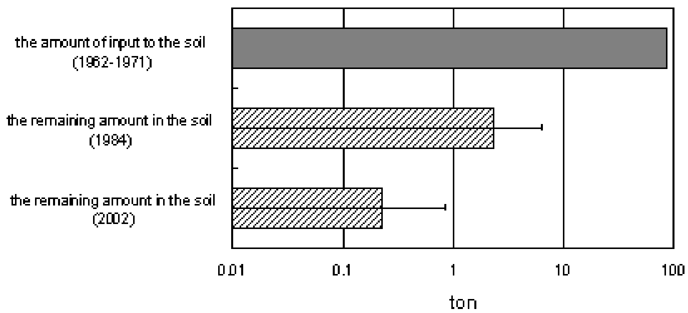

Fig. 4. The estimated the amount of input and remaining of HCH in the Yoneshiro River basin.

Acknowledgements

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