BEHAVIOR AND MASS BALANCE OF PCDD/DFs AND HERBICIDES IN PADDY FIELDS IN JAPAN

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Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are persistent and toxic contaminants in the environment. Herbicides, pentachlorophenol (PCP) and chloronitrophen (CNP), are reported to contain PCDD/DFs as impurities[1]. However, the behavior of PCDD/DFs, PCP and CNP in paddy fields, the correlation between PCDD/DFs and the herbicides, and their mass balance in river basins have never been elucidated. The objectives of this study are to investigate the temporal trends of the level and mass balance of PCDD/DFs and herbicides in paddy fields.

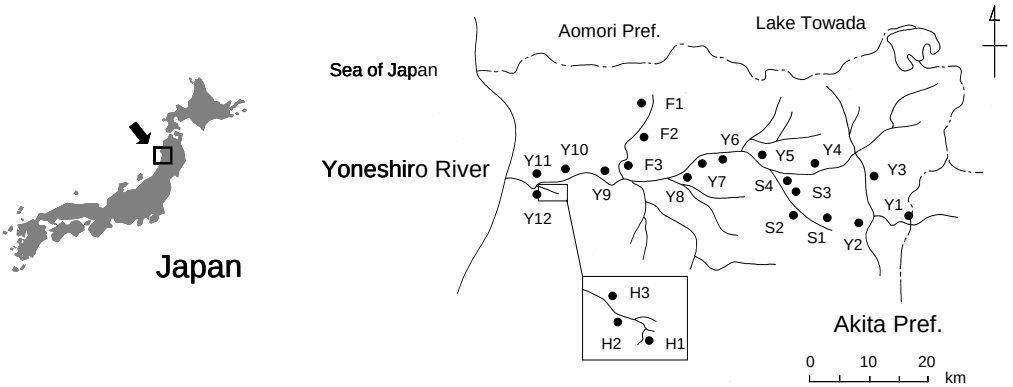

Fig. 1. Sampling sites in the Yoneshiro River basin.

Methods and Materials

Study area and sampling

Figure 1 shows the study area and sampling locations. Soil samples were collected from paddy fields located along the Yoneshiro River basin in 1982, 1984 (1980s), 2000, 2002 (2000s). The Yoneshiro River runs through paddy fields in the northern part of Akita Prefecture and flows into the Sea of Japan. Akita Prefecture is one of the prefectures of Japan where a large quantity of rice is produced and a large quantity of herbicides are applied to paddy fields. In the previous report[2], the number of sampling points was 8. In this report, 14 points were newly added. But three samples in 1980s (Y3, Y4, Y11) were not included in the analysis because of insufficiency of sample weight. One sample in 2000s (S4) could not be obtained due to urban development of this area.

Analysis method

The analysis method for PCDD/DFs was almost the same as that described in a previous report[2]. Toxic Equivalency Quantity (TEQ) concentrations were calculated using WHO-TEF (1998). The analysis method for PCP was according to The Analysis Manual for Endocrine Disrupters (Japanese Ministry of Environment). The analysis method for CNP was according to the method of Ono[3]. Free nitro-CNP (original chemical from) and free amino-CNP were analyzed and the sum of the both are CNP in this paper. Both herbicides were identified and quantified using GC/MS (SHIMADZU GC17A/QP5000) equipped with DB5-ms (Agilent).

Results and Discussion

PCDD/DF and herbicide levels in paddy soils

Table 1 shows the levels of PCDD/DF, PCP and CNP in the 1980s and 2000s. The average levels of TEQ and PCDD/DFs in the soil collected in the 1980s were 61 pg-TEQ/g and 86 ng/g, respectively. The average level of TEQ in the soil collected in the 2000s was 83 pg-TEQ/g and that of PCDD/DFs was 80 ng/g. The levels of TEQ and PCDD/DF did not decrease from the 1980s to the 2000s.

The average level of PCP in the soil in the 1980s was 9.6 ng/g, whereas the level in the 2000s was 4.6 ng/g. The average level of CNP in the soil in the 1980s was 48 ng/g, whereas the level in the 2000s was 9.3 ng/g. The average levels of PCP and CNP in paddy soils decreased from the 1980s to the 2000s. The level of CNP much decreased than that of PCP; this result seems to be due to the usage period of both herbicides. The usage period of PCP was from 1956 to 1974, whereas that of CNP was from 1965 to 1994; CNP was used in large quantities in the paddy fields in the 1980s.

Table 1. The levels of PCDD/DFs, PCP and CNP in the 1980s and 2000s.

	1980s (n=19)	2000s (n=21)
PCDD/DFs (pg-TEQ/g-d.w.)	3.4- 230 (avg. 61)	7.6- 320 (avg. 83)
PCDD/DFs (ng/g-d.w.)	6.9- 360 (avg. 86)	14- 220 (avg. 80)
PCP (ng/g-d.w.)	0.7- 39 (avg. 9.6)	n.d.- 20 (avg. 4.6)
CNP (ng/g-d.w.)	1.0- 190 (avg. 48)	n.d.- 45 (avg. 9.3)

Distribution in river basin

The distributions of PCDD/DFs, PCP and CNP in the 1980s and 2000s are shown in Fig. 2. The levels of TEQ and PCDD/DF (Figs. 2 (a), (b)) were high in the upstream and downstream regions of the river basin; they tended to be higher from upstream to downstream regions of narrow areas such as an affluent. The level of PCP decreased at each site from the 1980s to the 2000s and was high in the upstream and downstream regions (Fig. 2 (c)). CNP concentration decreased significantly in each site from the 1980s to the 2000s, and no area in the river basin showed a high CNP levels in the 2000s (Fig. 2 (d)). Moreover, PCP and CNP tended to be slightly higher from the upstream to downstream region of narrow areas such as an affluent. The tendency that herbicide concentrations in the downstream region are higher than those in the upstream region seems to be due to PCDD/DFs and herbicides transported by the river flow accumulate in paddy fields located downstream.

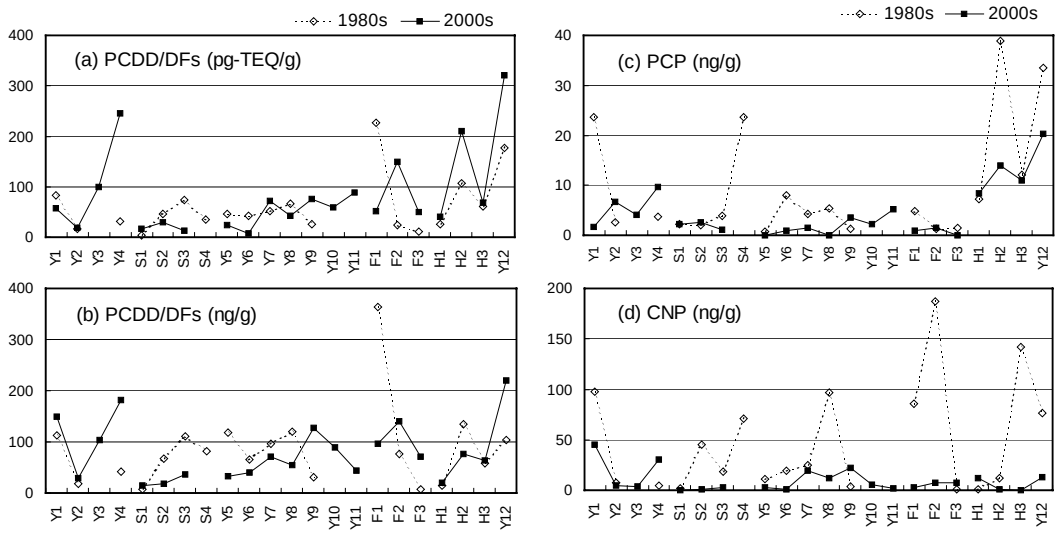

Fig. 2. Distribution of PCDD/DF, PCP and CNP levels in the soil of paddy fields in the Yoneshiro River basin in 1980s and 2000s. (Sites Y3, Y10 and Y11 were not analyzed in 1980s. Site S4 was not analyzed in 2000s.)

Characteristic PCDD/DFs in paddy soils

The homologues of TeCDDs and/or OCDD were predominant and common in all samples. The temporal change in homologue TeCDD was found to be larger than that in OCDD at many sites. The characteristic congeners were 1,3,6,8-TeCDD, 1,3,7,9-TeCDD, 1,2,3,6,8-PeCDD, HpCDD, OCDD and 2,4,6,8-TeCDF in all the samples. The levels of these congeners fluctuated in samples, whereas the congener composition within each homologue was relatively stable in almost all sites from the 1980s to the 2000s. Because PCP and CNP as commercial products contain these congeners as impurities, it is concluded that paddy field soil in the study area, as expected in the previous report[2], are polluted by PCDD/DFs originating from PCP and CNP.

Identification of sources and their contribution to PCDD/DFs

To identify the possible sources of PCDD/DFs in the paddy fields, principal component analysis (PCA) was newly applied to congener of all samples. PCA yielded two major principal components (PC); PC-1 and PC-2, which were identified to be the impurities in CNP and PCP, respectively. PCDD/DFs originating from combustion were not identified. This finding supports that in the previous paragraph.

The contributions of two sources to soil pollution were estimated by multiple regression analysis (MRA) using the congener profiles of PCDD/DFs originating from PCP and CNP. The contribution of PCDD/DFs originating from CNP was predominant at many sites, whereas that originating from PCP was predominant in the downstream region. The temporal change of PCDD/DFs originating from CNP was marked. This tendency seems to be due to the usage periods of PCP and CNP. PCP was hardly used in the 1980s, whereas CNP was largely used.

Mass balance of PCDD/DFs and herbicides in the Yoneshiro River basin

To understand the behavior and mass balance of PCDD/DFs, PCP and CNP in the Yoneshiro River basin, the amount of PCDD/DFs input to the river basin from herbicides was estimated from the quantity of herbicides usage[4] and their PCDD/DF contents[1, 5]. The remaining amount of PCDD/DFs in soil was estimated using PCDD/DF concentrations from PCP and CNP, which were obtained by MRA.

The mass balance of TEQ and PCDD/DFs is summarized in Fig. 3. In the case of TEQ, the amount of input was almost the same as the remaining amount. The amount of most TEQ originating from PCP and CNP applied to the paddy fields did not decrease. In the case of PCDD/DFs, the amount of input slightly decreased in the 1980s, then remained constant in the 2000s. PCDD/DFs originating from PCP decreased by one-half, whereas those originating from CNP decreased slightly.

The mass balance of PCP and CNP is summarized in Fig. 4. More than 99% of the herbicides applied to the paddy fields disappeared. Both herbicides decreased with time from the 1980s to the 2000s. Thus, most of the herbicides disappeared, whereas TEQ amount did not decrease. The long-term behavior of PCDD/DFs in river basins including paddy fields should be investigated.

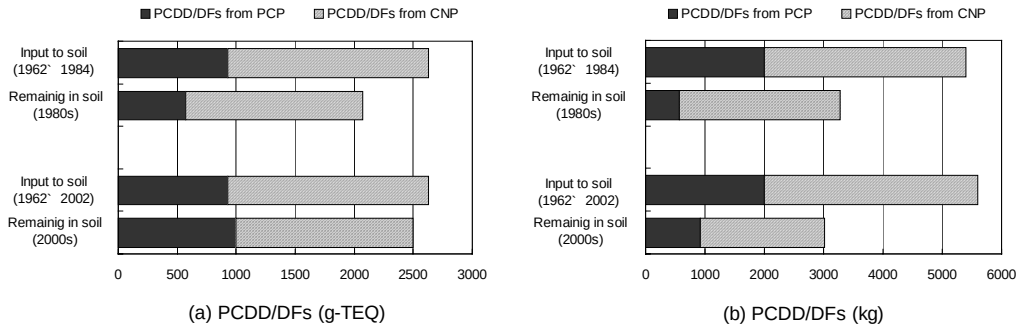

Fig. 3. Estimated input and remain of PCDD/DFs originating from PCP and CNP in the Yoneshiro River basin.

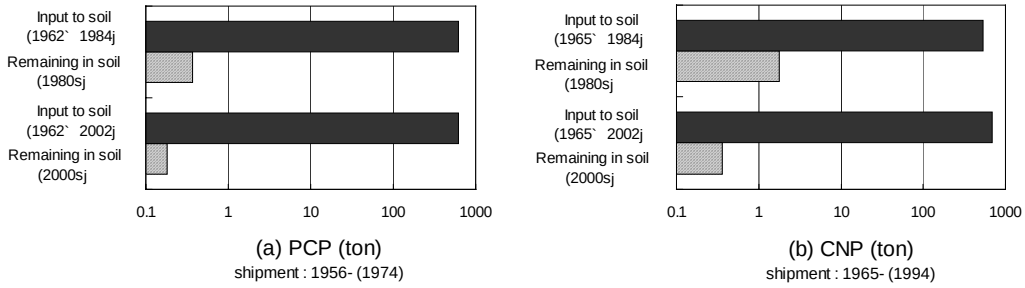

Fig. 4. Estimated input and remain of herbicides in the Yoneshiro River basin.

Acknowledgements

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