DIOXIN MASS BALANCE IN JAPANESE PADDY FIELDS

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Abstract
Mass balance of WHO-2,3,7,8,-TeCDD toxic equivalent quantity (TEQ) of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in Japanese paddy fields from 1958 to 2000 was estimated in order to predict the future contamination status. The cumulative input of TEQ to Japanese paddy fields from PCP, CNP, and combustion from 1958 to 2000 were estimated to be 250, 271 and 5 kg, respectively, indicating that PCDD/Fs were originated from PCP and CNP contributed over 95% of TEQ in paddy fields. The residual amount of TEQ in paddy fields in 2000 and the cumulative disappearance of TEQ from paddy fields were estimated to be as 105 kg and as 421 kg. Roughly 20% of TEQ in inputs are remained in recent paddy soils. On the other hand, approximately 80% of TEQ in inputs have disappeared over the past 40 years. Additionally, a quarter of TEQ in input have run off to the surrounding catchments during the past 40 years. As the amounts of PCDD/Fs input through the use of PCP and CNP were extremely large, TEQ in Japanese paddy soils will decrease gradually, and PCDD/F runoff from paddy fields to surrounding catchments will continue.

Introduction

PCDD/Fs are persistent toxic compounds ubiquitously found in the environment. PCDD/Fs are released into the environment mainly through the incineration of wastes. In addition, a variety of chlorinated compounds such as polychlorinated biphenyls (PCBs), pentachlorophenol (PCP), and 2,4,6-trichlorophenyl 4-nitrophenylether (chlornitrofen, CNP) contained considerable amounts of PCDD/Fs as impurities.[1-4] In Japan, PCP and CNP were commonly used as paddy herbicides in the past. PCP was used from 1958 to 1990, and CNP was used from 1965 to 1996. It is estimated that a total of 170×10^6 kg of PCP and 78×10^6 kg of CNP (active ingredient bases) were used.[5] PCDD/Fs released from PCP and CNP were estimated to be 120-440 and 180-270 kg-WHO-TEQ, respectively.[3,4] The annual emissions of PCDD/Fs from combustion in 1997 were estimated to be 6.9 to 7.1 kg-WHO-TEQ $year^{-1}$.[6] PCDD/Fs emissions from PCP and CNP were extremely large compared with those from combustion.

According to a nationwide survey performed by the Ministry of the Environment and the Ministry of Agriculture, Forestry and Fisheries of Japan, TEQ in paddy soils was significantly higher than that in uncultivated soils.[7,8] Additionally, PCDD/F congeners such as OCDD and 1,3,6,8-/1,3,7,9-TeCDD are major PCDD/Fs in PCP and CNP (3-6) as impurities, respectively, and are accumulated in surface sediments and fish in Japan.[9,10] It can be indicated that PCDD/Fs from these herbicides applied to paddy fields have flowed out into the surrounding catchments. Thus, paddy fields have played an important role as a secondary source of PCDD/Fs in the aquatic environment for half a century. It is therefore important to estimate the mass balance of PCDD/Fs and their temporal trends using associated information such as shipments of PCP and CNP, TEQ contents in these herbicides, area of paddy fields, half-lives, and so on for the prediction of future contamination status. In this paper, mass balance of TEQ in Japanese paddy fields from 1958 to 2000 was estimated.

Materials and Methods

Parameters for estimation of mass balance of TEQ in Japanese paddy fields from 1958 to 2000 are shown on Table 1. First, we estimated cumulative input of TEQ to Japanese paddy fields from PCP, CNP, and combustion with the following expressions:

$$Ih = \sum_{n=1958}^{2000} (Ch \times Uh) \qquad (1)$$

Table 1. Parameters for PCDD/Fs(TEQ) mass balance estimation

Parameters	Value	Ref.
TEQ in PCP (from 1958 to 1990)	1.5 μg g^{-1}	3, 4
Use of PCP (from 1958 to 1990, active ingredient bases)	170×10^6kg	5
TEQ in CNP (from 1965 to 1981)	4.6 μg g^{-1}	3, 4
TEQ in CNP (from 1982 to 1994)	0.012 μg g^{-1}	3, 4
Use of CNP (from 1965 to 1994, active ingredient bases)	78×10^6kg	5
Atmospheric deposition flux of TEQ in 1999	7500 ug km^{-2} $year^{-1}$	8
Annual municipal wastes (from 1958 to 2000)	2,000~40,000 $\times 10^6$ kg $year^{-1}$	11
Area of paddy fields	20×10^3 ~ 30×10^3 km^2	12
Half-lives in paddy soil	16.3 year	13
Runoff	2% $year^{-1}$	9
Depth of the plow layer	14.6 cm	14
Soil density	1.2 g cm^{-3}	14

$$Ic = \sum_{n=1958}^{2000}[(F_{1999}/W_{1999}) \times W_n \times S_n] \qquad (2)$$

where *Ih* is input of TEQ from PCP and CNP (kg-TEQ), *Ch* is the arithmetic mean of TEQ by active ingredients in PCP and CNP (μg-TEQ kg^{-1}), *Uh* is usage of PCP and CNP in Japan (kg), *Ic* is input of TEQ from combustion (kg-TEQ), *F* is the arithmetic mean of TEQ atmospheric deposition flux in 1999 obtained from a nationwide survey (μg-TEQ km^{-2} $year^{-1}$), *W* is the amount of municipal waste in year *n* (kg $year^{-1}$), and *S* is the area of paddy fields in year n (km^2). Next, we estimated the residual amount of TEQ in Japanese paddy fields in each year with the following expressions:

$$R_n = Ih_n + Ic_n + [R_{n-1}/2^{1/\tau} \times (1 - Rc_n) \times (1 - Rr)] \qquad (3)$$

$$Rc_n = (S_{n-1} - S_n)/S_{n-1} \qquad (4)$$

where *Rn* is the residual amount of TEQ in paddy fields in year n (kg-TEQ), τ is the half-life of TEQ in paddy soils, *Rcn* is the proportion of curtailment of paddy field area in year n (%), and *Rr* is the ratio of annual runoff, assumed to be 2%/yr. Finally, we estimated the cumulative disappearance of TEQ from Japanese paddy fields by the curtailment of paddy fields, runoff with soil, and unknown processes with the following expressions:

$$Dc = \sum_{n=1958}^{2000}(R_{n-1} \times Rc_n) \qquad (4)$$

$$Dl = \sum_{n=1958}^{2000}[R_{n-1}/2^{1/\tau} \times (1 - Rc_n) - [R_n \times (1 - Rr)]] \qquad (5)$$

$$Du = \sum_{n=1958}^{2000}[(Ih_n + Ic_n) - (R_n + Dc_n + Dl_n)] \qquad (6)$$

where *Dc* is the cumulative disappearance of TEQ by the curtailment of paddy fields (kg-TEQ), *Dl* is the cumulative disappearance of TEQ by runoff with soil (kg-TEQ), *Du* is the cumulative disappearance of TEQ by unknown processes (kg-TEQ). The curtailment of paddy fields means that the paddy fields were converted to other land uses, such as upland farms and residential land. This estimate assumes that TEQ do not disappear after land use is changed.

The temporal trend of mean TEQ originating from PCP, CNP, and combustion in Japanese paddy soils from 1958 to 2000 were also estimated with the following equation:

$$Cs_n = R_n/S_n/H/D \qquad (7)$$

where *Csn* is the TEQ in paddy soils (pg-TEQ g^{-1} dry weight), *H* is the depth of the plow layer, and *D* is the soil density obtained from a nationwide survey.

Results and Discussion

Input of TEQ to Japanese paddy fields

Temporal change in the input of TEQ to Japanese paddy fields from PCP, CNP, and combustion from 1958 to 2000 are shown in Fig.1. The trend of the inputs of TEQ from PCP and CNP were well agreed with their usage. The cumulative input of TEQ to Japanese paddy fields from PCP, CNP, and combustion from 1958 to 2000 were estimated to be 250, 271 and 5 kg, respectively, and that most TEQ originated from PCP and CNP (Table 2).

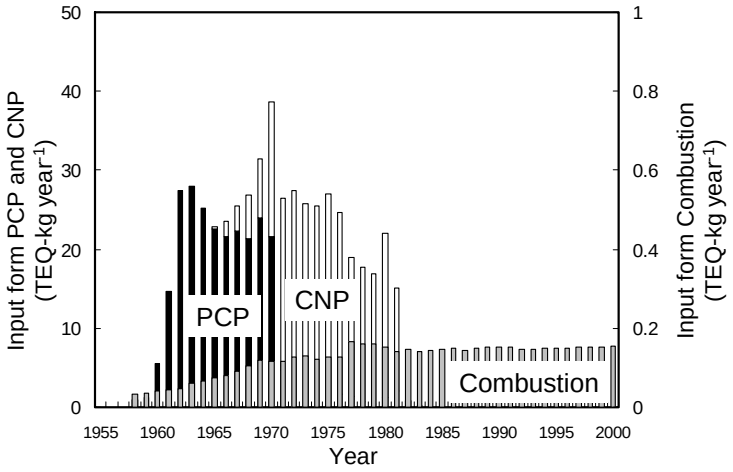

Fig. 1 Temporal changes in input (kg-TEQ $year^{-1}$) to Japanese paddy field by PCP, CNP and combustion

Mass balance of TEQ in Japanese paddy fields

We estimated the residual amount of

TEQ in paddy fields in 2000 as 105 kg, and the cumulative disappearance of TEQ from paddy fields as 421 kg. The residual amount TEQ in paddy fields from 1999 to 2002 based on a nationwide survey was calculated to be 138 ± 124 kg (mean ± S.D.). [7] Our estimate of the residual TEQ in paddy fields in 2000 agrees well with the results of the survey, indicating that roughly 20% of TEQ in inputs are residues in recent paddy soils. On the other hand, approximately 80% of TEQ in inputs have disappeared over the past 40 years. Approximately 20% of TEQ in inputs have disappeared by the curtailment of paddy fields. The policy of curtailing paddy fields has been promoted by the Japanese government since the 1970s, and approximately 30% of paddy fields have been curtailed up to the present, indicating that our estimate is reasonable, and the curtailing of paddy fields cannot be ignored in estimates of the TEQ mass balance in Japanese paddy fields. Additionally, a quarter of TEQ in input have run off to the surrounding catchments during the past 40 years. As a result, PCDD/Fs originating from PCP and CNP have accumulated everywhere in Japanese sediments. [9,10]

Table 2. Mass balance of TEQ (kg) in Japanese paddy fields from 1958 to 2000

Source	Cumulative Input	Residue in 2000	Disappererance (1958-2000)			
			Total	Curtailment of Paddy Field	Runoff	Unknown
PCP	250	35	215	72	67	76
CNP	271	68	203	72	57	74
Combustion	5	2.4	2.6	1.1	0.6	0.9
Total	*526*	*105*	*421*	*145*	*125*	*151*

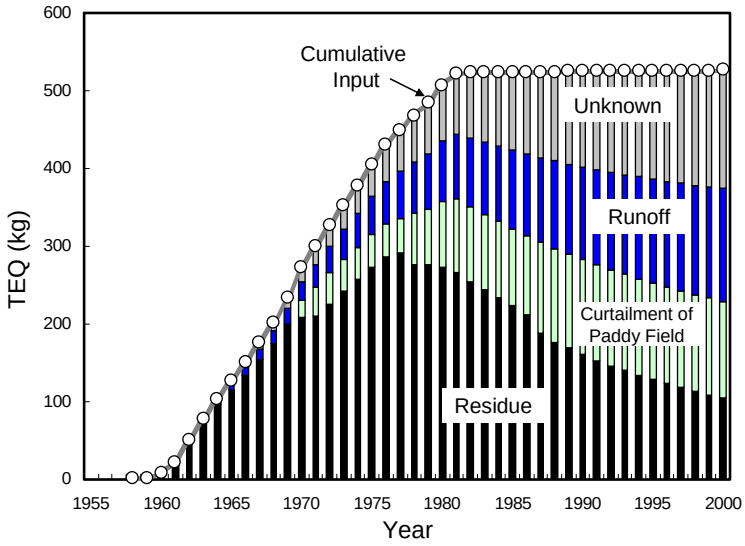

Fig. 2 Temporal changes in cumulative input, residual amount, disappearance (kg-TEQ) in Japanese paddy field

The estimated TEQ increased greatly during the 1960s, but has been decreasing gradually since around 1980 (Fig. 3). The TEQ in paddy soils from 1999 to 2002 based on a nationwide survey was calculated to be 39 ± 35 pg-TEQ g^{-1} (mean ± S.D.).[7] Our estimate of TEQ in paddy fields in 2000 (29.5 pg-TEQ g^{-1}) agrees well with the results of the survey. Further, PCDD/Fs originating from PCP and CNP contributed over 95% of TEQ (Fig. 3). These results indicate that the estimated temporal trends of TEQ and contributions by PCDD/F sources in paddy fields from 1958 to 2000 agree well with the results of the preserved samples analysis. [13]

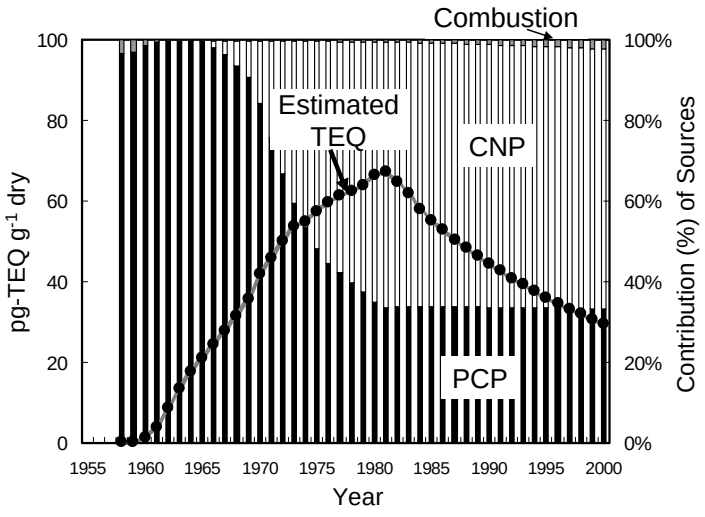

Fig. 3 Estimated temporal changes in TEQ (pg-TEQ g^{-1}) and contributions (%) of PCDD/F sources in Japanese paddy fields

In Japan, the use of PCP and CNP was banned in the 1990s, and the content of PCDD/Fs in agricultural chemicals is controlled. Emission controls on waste incinerators and design improvements have been imposed since the late 1990s by the Japanese government. Therefore, further PCDD/F contamination of paddy fields should not occur, and TEQ in Japanese paddy soils will decrease gradually. PCDD/F runoff from paddy fields to surrounding catchments will also reduce but continue. Hence we should develop techniques to reduce the runoff of paddy soils to reduce PCDD/F contamination in the aquatic environment.

Acknowledgements
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