TEMPORAL TRENDS FOR DIOXINS-RELATED AGROCHEMICALS IN SEDIMENTS IN A LARGE-SCALE RICE-PRODUCING AREA, NIIGATA, JAPAN

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Introduction

Japanese people have historically eaten rice as the main grain constituent in their diet. In the past 50 years, a larger amount of agrochemicals have been applied to Japanese rice fields to increase rice production. Masunaga et al. reported that common Japanese agrochemicals such as pentachlorophenol (PCP) and chloronitrophen (CNP) used in rice fields in the past contain dioxins as impurities [1]. Since Niigata Plain is the largest rice-producing area in Japan, the soil and/or sediment in the lower basin in Niigata Plain could be highly polluted. In the previous study, we measured the age of a sediment core and the amount of dioxins (PCDD/DFs) in Toyano Lagoon and estimated the historical trend and the sources of dioxin[2]. Most of the sources of dioxin in Toyano Lagoon sediment were PCP and CNP. The aims of this work are to quantify the extent, clarify the historical trends of CNP and PCP pollution in the Toyano Lagoon sediment and consider the interrelation between them.

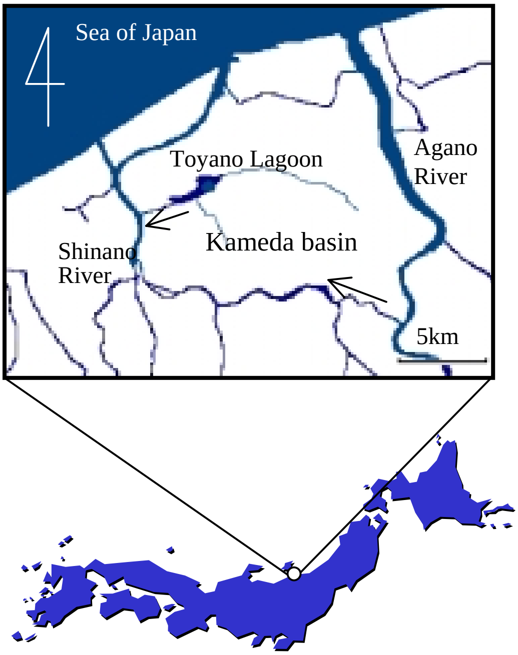

Figure 1 Sampling Site.
Arrows mean flow direction.

Method and Materials

Sediment Core

A sediment core, which was a cylindrical sample with a diameter of 20cm and a length of 80cm, was obtained from the northern part of Toyano Lagoon. Toyano Lagoon is located in a suburban area in Niigata City, between the lower basin of the Shinano River and Agano River in Niigata

Plain (Fig.1). Toyano Lagoon receives water flow from rice fields that are irrigated from the Shinano and Agano Rivers, and wastewater from households. The sampling point was selected from the area where dredging had not been carried out to date. The sample core was sliced into 2-cm-thick disks. The average sedimentation rate estimated using the Pb-210 method and Cs-137 method was 0.32 g cm^{-2} $year^{-1}$.

Analysis

1) PCDD/DFs

The samples were air dried and grounded to fine powder. Sample of 10 - 35 g were used for analysis. The analytical method was according to the manual of the Japanese Ministry of Environment. The measurement of PCDD/DFs was performed by HR-GC/HR-MS (Hewlett Packard HP6890/JEOL JMS-700). Detailed analytical procedure was described in the previous paper[2].

2) Agrochemical analysis

The analysis methods were according to the manual of the Japanese Ministry of Environment for PCP, and to the method of Ono[3] for CNP. The measurement of each agrochemical was performed by GC/MS (SHIMADZU GC17A/QP5000).

Results and considerations

1) Temporal trend of PCP and PCP concentrations

Table 1 and Fig. 2 show PCP and CNP concentrations, along with estimated sedimentation age of each sliced core.

PCP concentration significantly increased in 1960s, reached the maximum in 1968, decreased after 1968, and has continued decreasing in recent years. Although nitro-CNP was not detected in the same period at all, amino-CNP was detected. The concentration of amino-CNP reached the maximum in 1982 and then decreased thereafter.

Because the production of PCP in Japan was stopped in 1973, the subsequent circulation amounts were very few. However, in this study PCP was detected in the sediment layer after

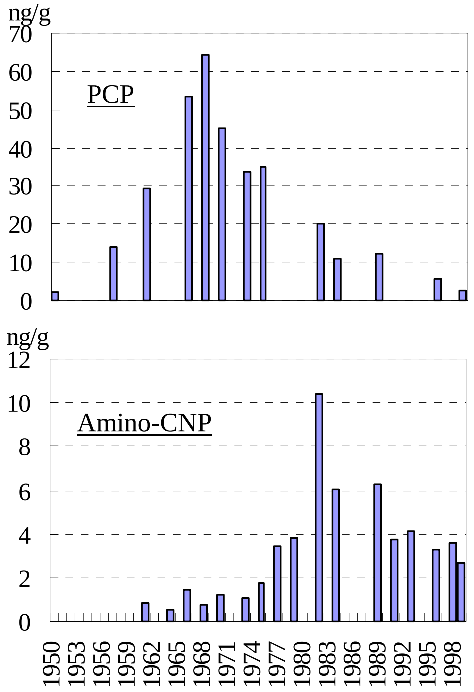

Figure 2 Temporal trends of PCP and CNP in sediment core of Toyano Lagoon

Table 1 Time Trends of Concentration in Sediment Core

Depth (cm)	Date (year)	Consentoration (ng/g) PCP	Amino-CNP
44-46	1950	2.4	-
38-40	1957	14	-
34-36	1961	29	0.85
32-34	1964	-	0.51
30-32	1966	53	1.4
28-30	1968	64	0.8
26-28	1970	45	1.3
24-26	1973	33	1.1
22-24	1975	35	1.7
20-22	1977	-	3.5
18-20	1979	-	3.8
16-18	1982	20	10.0
14-16	1984	11	6.0
10-12	1989	12	6.3
8-10	1991	-	3.8
6-8	1993	-	4.2
4-6	1996	5.7	3.30
2-4	1998	-	3.6
0-2	1999	2.7	2.7

1975. This seems to be due to the remaining PCP and CNP in paddy soils or canal sediments, which flowed into Toyano Lagoon.

2) Contribution to PCDD/DFs amounts

In the previous study[2], we estimated the contribution rate of each pollution source to PCDD/DFs. To identify the sources of PCDDs/DFs, and to calcurate the amount of PCDD/DFs from each soruce, Principal Component Analysis (PCA) was performed to the congener concentrations.

PCDD/DFs from PCP and CNP predominated most of concentration, and the contribution of all the other sources were about 0.19 - 0.79% only.

The concentration of PCDD/DFs in Toyano Lagoon estimated from PCP and CNP are shown in Fig. 3 with PCP and CNP amounts in sediment and their shipment amount into Kameda basin.

Maximum temporal trends in PCDD/DFs concentrations from PCP and CNP were observed in 1964 and 1977, respectively, after which the concentrations decreased.

The concentration of PCDD/DFs accumulated in the sediment was higher than those of CNP and PCP. Shipment amount of the two agrochemicals in Kameda baisn showed similar temporal trend with the PCDD/DFs from PCP and CNP .

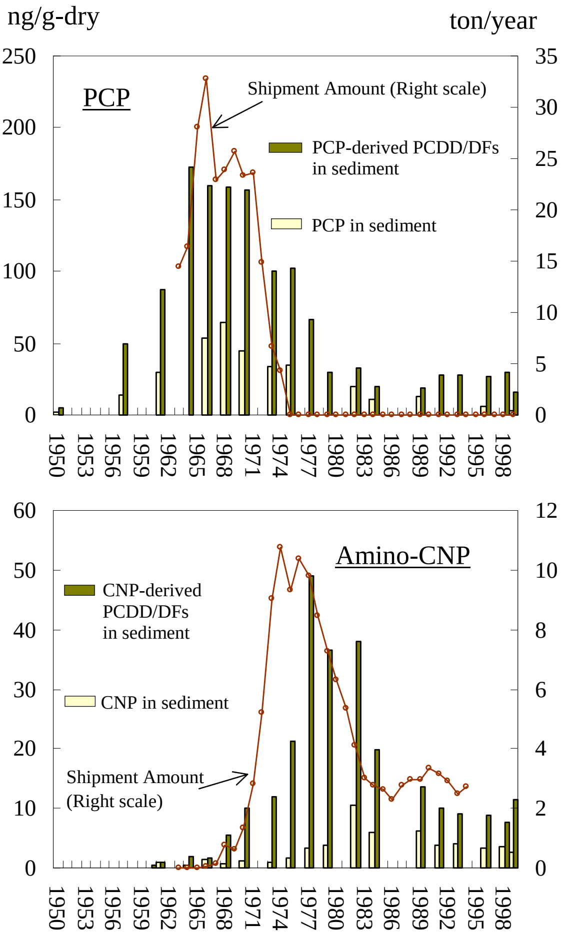

Figure 3 Comparison of PCP and CNP, PCDD/DFs from agrochemicals, and shipment amount

Mass balance

We compared PCP and CNP shipment amount and PCDD/DFs in them at the time of shipment in Kameda basin with the PCP and CNP depositions and PCDD/DFs ones derived from them in Toyano Lagoon.

1) Calculation method

The calculation parameters of mass balance are shown in Table 1. The inputs of PCP and CNP correspond to the shipment amount into Kameda basin[4]. The input of agrochemical-derived PCDD/DFs was calculated from the shipment amount and their concentrations in the agrochemicals obtained from the literature[5, 6]. To estimate the amount of each compound deposited in Toyano Lagoon, we used following equation:

$$Total\ deposition = \sum_i (Ci \times toyano\ lagoon\ area \times soil\ density \times 2cm)$$

where *Ci* is the observed value, and other parameters are shown in Table 1. The concentrations in periods when PCP and CNP were not measured were assumed by linear or exponential approximation.

The deposition in the paddy soils of Kameda basin was calculated by multiplying the concentration of each compound in Toyano Lagoon surface by the present paddy field area, soil density, and soil depth.

2 Estimation result

The estimated mass balance values are shown in Table 2. The amounts of deposition of PCP and CNP in Toyano lagoon and paddy soils were very few compared with those of their input in Kameda basin. It is possible that most of PCP and CNP flowed out or decomposed within Kameda basin. In contrast to the two agrochemicals, the rate of diposition of PCDD/DFs in Toyano Lagoon and paddy fields in Kameda basin is much higher. The remaining amount of PCDD/DFs were considered to be discharged to the Shinano River via a small channel.

Table 2 Calculation parameters of mass balance

Input

	shipment amounts[4]	concentrations of PCDD/DFs in Herbicides[5)6)]		
PCP (n=14)	240ton		3300	µg/g
CNP (n=14)	130ton	before 1981	7000	µg/g
		after 1982	1200	

parameters @

	PCP, CNP	PCDD/DFs
concentration in sediment	observed value	estimated value
soil density	$1.0 g/cm^3$	
paddy field area	4010ha	
soil depth	15cm	
toyano lagoon area	160ha	
sediment sample thick	2cm	

Table 3 Estimated result of mass balance

	input to Kameda basin	Toyano lagoon	paddy felids
PCP	240000 (100)	14 (0.0059)	16 (0.0066)
CNP	130000 (100)	1.8 (0.0014)	16 (0.012)
PCDD/DFs from PCP	780 (100)	48 (6.8)	170 (22)
PCDD/DFs from CNP	660 (100)	8.9 (1.4)	56 (8.5)

Input or remaining amounts of each compounds (kg) and the deposition rate (%)

Acknowledgements

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