TIME TRENDS AND SOURCE FOR DIOXINS IN SEDIMENTS IN A LARGE-SCALE RICE PRODUCTION AREA, NIIGATA, JAPAN

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Introduction

The Japanese 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. However, Masunaga et al. reported that common Japanese agrochemicals such as pentachlorophenol (PCP) and chloronitrophen (CNP) that have been used for rice fields in the past contained dioxins as impurities [1,2]. In the previous work, we found that soil in rice fields in the lower basin was much more contaminated than that in the upper basin. This is probably because that dioxins distributed in the rice fields in the upper basin flowed out into the river and came back into the rice fields in the lower basin, where they accumulated [3]. Since Niigata Plain is the largest rice production area in Japan, the soil and/or sediment in the lower basin in Niigata Plain could be polluted seriously. The aim of this work is to quantify the extent, clarify historical trends and identify the sources of dioxin pollution in the lower basin in the large-scale rice production area.

Methods and Materials

Sediment Core

A sediment core, which was a cylindrical sample with a diameter of 20cm and a length of 80cm, was taken from the northern part of Toyano Lagoon in December 2000. Toyano Lagoon is located in a suburban area in Niigata City, and in the lower basin of the Shinano River and Agano River in Niigata Plain (Fig.1). Toyano Lagoon receives the flow from rice fields that are irrigated by the Shinano River and Agano River, and water 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, and the average sedimentation rate estimated using the Pb-210 method and Cs-137 method was 0.32 g cm^{-2} $year^{-1}$. Sampling and estimation for the sedimentation rate was consigned to Metocean Environment Inc.

Analysis

After the addition of ^{13}C-labeled internal standards, dried sediments (about 30g) were extracted with toluene in a Soxhlet apparatus for 16 hours. Sulfur contained in the sediments was removed using Copper tips during the extraction. Extracts were then treated with concentrated sulfuric acid and further purified using a series of silica gel columns and active carbon-impregnated silica gel columns. The final PCDDs/DFs and co-PCBs fractions were concentrated to 100μL and spiked with ^{13}C-labeled recovery standards for HRGC/HRMS (JEOL JMS-700) analysis. The CPSil-88 for DIOXINS (CHROMPACK) and HP-5 (Hewlett Packard) columns were used for quantification of PCDDs/DFs,

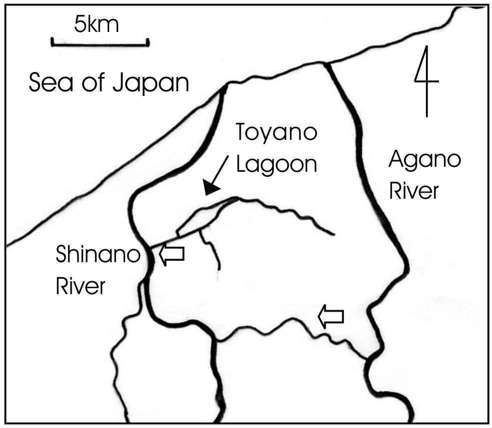

Figure 1. Sampling Site. Outline arrows mean direction.

and the DB-5 (Hewlett Packard) column was used for co-PCBs. One hundred thirty-six PCDD/DFs congeners (from tetrachloro to octachloro) were separated and quantified as 108 gas chromatographic peaks. Twelve congeners of co-PCBs (four congeners for non-ortho PCBs and eight congeners for mono-ortho PCBs) were also quantified.

Statistical Procedure

Principal component analyses of the data were performed using software package «STATISTICA» (Stat-Soft, Inc).

Results and Discussion

Time Trend

The average rates of average were 81±29 % for 2,3,7,8-congeners and 61±14 % for co-PCBs. TEQ values and concentrations of PCDDs/DFs and co-PCBs along with estimated sedimentation age for each sliced core are shown in Table 1 and Fig. 2. Total TEQ significantly increased in 1950s, maximized in 1968, rapidly decreased in 1970s, and became almost constant after 1980s. In 1968, TEQ was 300 pg-TEQ/g-dry, which was one of the highest levels for sediments in rivers and lakes ever reported in Japan. Although the time trends of PCDDs and PCDFs were similar to total TEQ, TEQ of co-PCB was different from them. TEQ of co-PCBs significantly increased in 1960s, maximized in 1973, decreased after 1973, and became constant after 1990s. Since the contribution of co-PCBs to total TEQ was small, those of PCDDs/DFs are mainly discussed in this report hereafter.

Identification of the Sources

To identify the sources of PCDDs/DFs, Principal Component Analysis (PCA) was performed to the congener concentrations. A total of 98 gas chromatographic peaks and 12 slices of the sediment cores were regarded as variables and cases, respectively, excluding 44 - 46 cm and 46 - 48 cm slices from cases because of their small concentrations and excluding the peaks below the detection limit from variables. The analysis revealed three major principal components (PCs) whose eigenvalues were more than five. The cumulative proportion of the three PCs was 84 %. Characteristic congeners of PC1 were highly chlorinated (hexa- to octa-) DDs/DFs without OCDF. These ccorrespond well with the impurities in PCP. Characteristic congeners of PC2 were less chlorinated DDs, such as 1368-TCDD,

Table 1 Time Trends of Concentration and WHO-TEQ in Sediment Core

Depth	Date	Concentration (pg/g-dry)			WHO-TEQ (pg-TEQ/g-dry)			
(cm)	(year)	PCDD	PCDF	Co-PCB	PCDD	PCDF	Co-PCB	Total
0 - 2	1999	39000	2000	3600	39	19	2.9	61
2 - 4	1998	36000	2000	3600	46	16	2.7	64
4 - 6	1996	35000	1900	3600	40	13	2.1	55
6 - 8	1993	35000	2000	3400	42	13	2.1	57
8 - 10	1991	37000	2100	5700	46	15	3.1	64
10 - 12	1989	45000	2600	7400	45	26	4.3	76
14 - 16	1984	53000	3100	7000	51	26	4.9	82
18 - 20	1979	87000	3600	8100	65	31	5.0	101
24 - 26	1973	107000	5400	29500	135	75	9.9	219
28 - 30	1968	157000	7100	10600	205	93	3.1	300
34 - 36	1961	148000	5500	2000	176	76	0.79	253
38 - 40	1957	39000	2200	970	57	21	0.41	78
44 - 46	1950	4700	230	370	9.7	4.7	0.12	15
46 - 48	1946	900	40	- [a]	6.7	2.0	- [a]	- [a]

a) not measured

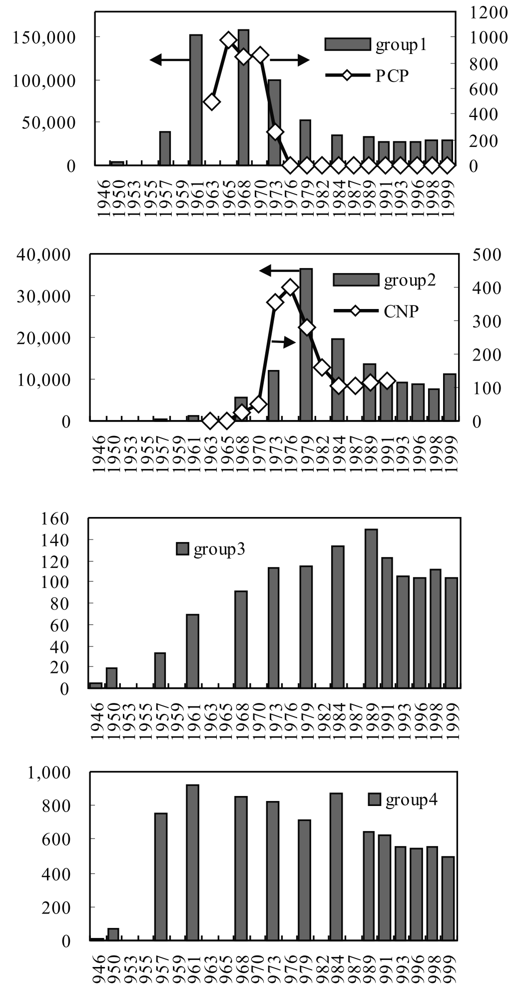

Figure 3. Time Trend of Each Congener Group Determined by Principal Component Analysis and Shipment Amount of PCP and CNP.

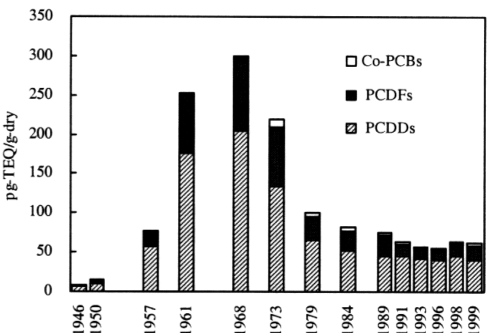

Figure 2 Time Trend of TEQ for Sediment Core of Toyano Lagoon.

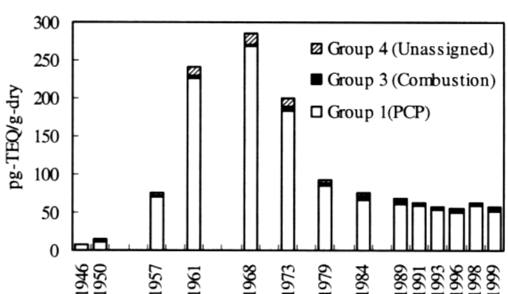

Figure 4 Time Trend of Contribution of Each Source to TEQ of PCDDs/DFs.

1379-TCDD. These agreed well with the impurities in CNP. The characteristic of PC3 was that the factor loadings for less-chlorinated DFs was relatively high. This characteristic was considered to be due to combustion sources.

Grouping of congeners

To clarify the time trends of each principal component, all congeners were classified into four groups, namely Groups 1, 2 and 3: include congeners whose factor loading for PC1, 2 and 3 was more than 0.7, and Group 4: include congeners whose factor loading for any PC (1-3) was less than 0.7. In Group 4, congeners from more than two sources were classified. The temporal changes of the sums of congener concentrations for each group and of the shipment amount of the ingredient for PCP and CNP in Niigata Prefecture [4] are shown in Fig. 3. The changes in concentration for Group 1, that is increasing significantly in 1950s, having the maximum in 1968, and decreasing in 1970s, was in good agreement with the shipment amount of PCP as shown in Fig. 3(a). The changes in concentration for Group 2, that is increasing in the latter 1960s, reaching the peak in 1979, and then decreasing in 1980s, was in agreement with the shipment amount of CNP as shown in Fig. 3(b). The concentration of Group 3 continued to increase until 1989, and then slightly decreased. This behavior may represent the time trends of the PCDDs/DFs emitted from combustion sources such as municipal incinerators. Group 4 did not show any particular tendency.

Contribution to TEQ

The temporal change of TEQ for each group is shown in Fig. 4. PCP (Group 1) was found to predominantly contribute to TEQ throughout the observation. The contribution of CNP (Group2) to TEQ was zero because no 2,3,7,8- congener was assigned to CNP (Group 2). However, unassigned congeners of Group 4 may include those from CNP. The contribution of combustion was maximum in 1989, but its contribution is much less than that of PCP. In this work, the contributions of CNP and combustion were much less than those determined in the study on sediments in Tokyo Bay [5] or Lake Shinji [2], Japan. Although the reason for such difference has not been clarified at present, the situation of agrochemical use for each region may affect the results. In conclusion, the sediment of the lower basin of the large-scale rice production area in Japan was extremely polluted by dioxins mainly discharged as impurities of PCP during the past 40 years. The effects of dioxin pollution on aquatic life and land animals including humans who eat aquatic life growing in that area have to be investigated carefully.

Acknowledgements

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