

Measurement of PCDDs and PCDFs in sediment samples from Lake Kasumigaura, Japan

Takeo Sakurai¹, Noriyuki Suzuki¹ and Junko Nakanishi²

¹Faculty of Engineering, University of Tokyo

²Environmental Science Center, University of Tokyo

1,2 7-3-1, Hongo, Bunkyo-ku, Tokyo 113, Japan

INTRODUCTION

Lake Kasumigaura is a freshwater lake which used to be a part of the sea about 600 years ago. The surface area is 220 km² and the average depth is 4 m. Its catchment area is 2,200 km² in which 850,000 people reside, and 42% of the area is agricultural land.

Lake Kasumigaura was chosen as the sampling field for the following reasons. First, it is the second-largest lake in Japan. Secondly, more than 20% of its catchment area consists of paddy fields to which large amounts of herbicide are applied, and herbicide impurities are known as one of the major sources of PCDD/Fs. Thirdly, the distance between the lake and Tokyo is about 70 km, so that airborne PCDD/Fs from the Tokyo area may impact the Lake Kasumigaura sediment. In this study, the concentrations of PCDD/Fs in 4 sediment samples were determined, and were subject to isomeric comparison with those from a paddy field sample.

EXPERIMENTAL SECTION

Sampling

The sampling sites are shown in Figure 1. Four sampling points (LC, TK, TT and TZ) in Lake Kasumigaura were selected because of their geographic representativeness. At each point, a surface sediment sample was collected in November 1994. All sediment samples were dark-colored mud. The TZ sample was slightly sandy. A paddy field soil near the lake was sampled in July 1993.

Analytical procedure

PCDDs and PCDFs with 4 to 8 chlorine atoms were subject to analysis.

Sediment samples were air-dried, manually ground, and sieved through 2-mm mesh. After addition of ¹³C-labeled standard compounds (Cambridge Isotope Laboratories), 50 to 200 g

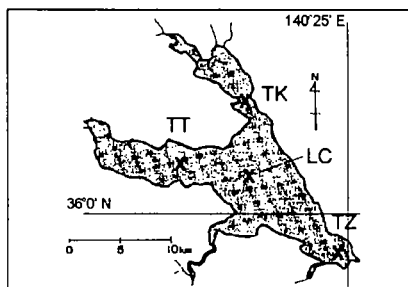


Figure 1 Lake Kasumigaura and sediment sampling points

of samples was extracted with toluene for 20 hours using a Soxhlet/Dean-Stark extractor¹). Concentrated extracts were dissolved in *n*-hexane and treated with aqueous potassium hydroxide and concentrated sulfuric acid. Then the extracts were treated with copper to remove sulfur, and passed through a series of column chromatographic clean-up steps of silica gel, basic aluminum and activated carbon impregnated in silica gel.

Identification and quantification were performed using high-resolution gas chromatography/high-resolution mass spectrometry. Separation was achieved on a HP 5890II-plus instrument equipped with a DB-5 (60m x 0.25 mm i.d., J&W Scientific) and a DB-17 (60m x 0.25 mm i.d., J&W Scientific) column. DB-17 was used to quantitate 2,3,7,8-substituted compounds that are not separable on DB-5 and some other compounds that were interfered on DB-5. Detection was carried out on a VG AutoSpec-Ultima system in electron impact mode at the resolution $R > 10,000$ (10% valley).

Peaks were assigned according to a report by Ryan *et al.*²). Detection and quantification followed the criteria in U.S. EPA Method 1613³). Several peaks of lower concentrations within $\pm 30\%$ of the theoretical ion ratio were also quantified. Detection limits were 0.1~0.3 pg/g dry weight. One blank sample was analyzed for every three samples. Blank samples gave no or negligible PCDD/F peaks.

RESULTS AND DISCUSSION

Table 1 gives a summary of results obtained. Figure 2 shows the share of each dioxin/furan congener group in total dioxin/furan concentration. Results of an urban soil sample are included in Figure 2 for comparison. In sediment and paddy field samples, PCDDs comprise more than 90% of the total PCDD/F concentrations, compared to 57% in the urban soil sample. Homologue profiles of dioxins are very similar among sediment samples except for the TZ sample which shows a higher contribution of lower-chlorinated congener groups. In

Table 1 PCDD, PCDF and I-TEQ concentrations (pg/g dry weight) and ignition loss (% dry weight) of sediment and paddy-field samples

sample	lake sediment				paddy field	internal standard recovery*1
	LC	TK	TT	TZ		
total	6,546	12,014	5,493	1,270	1,607	
Σ PCDFs	517	767	470	115	100	
Σ TCDFs	101	108	84	26	47	77~85%
Σ PeCDFs	84	79	81	21	18	72~105%
Σ HxCDFs	106	162	104	24	14	67~92%
Σ HpCDFs	149	274	128	28	14	57~85%
OCDF	77	145	72	16	7	-*2
Σ PCDDs	6,029	11,247	5,023	1,155	1,507	
Σ TCDDs	416	617	377	235	963	70~84%
Σ PeCDDs	106	115	100	42	97	75~102%
Σ HxCDDs	288	456	203	39	27	79~108%
Σ HpCDDs	1,028	1,660	711	130	69	68~78%
OCDD	4,191	8,400	3,633	710	351	70~90%
I-TEQ	20.16	30.51	16.86	3.76	2.52	
ignition loss	17.4%	18.8%	15.8%	4.5%	3.9%	

*1 range of internal standard(s) recovery within each congener group

*2 ¹³C-OCDF was not used as an internal standard.

the paddy field sample, TCDD is predominant. As for furans, the 4 sediment profiles also appear similar in contrast with those of the paddy field and urban soil samples. In the paddy field sample, TCDF is the dominant congener group. The values and homologue profiles of PCDD/F concentration in the sediment samples are generally in good agreement with those reported by the Japanese Environment Agency⁴).

Normalized to ignition loss, the ranges of total furan and dioxin concentrations in sediment and paddy field samples are 2,534 ~ 4,074 and 25,437 ~ 59,719 pg · (g ignition loss)⁻¹, respectively.

Isomer patterns of TCDF are shown in Figure 3-1, including the results of the urban soil sample. They are shown in percentage of total TCDFs. Lake sediment samples show a similar pattern. One can notice the predominance of 2,4,6,8-TCDF in the paddy field sample. 2,4,6,8-TCDF is also the most abundant isomer in all sediment samples. Yamagishi *et al.* detected 2,4,6,8-TCDF in

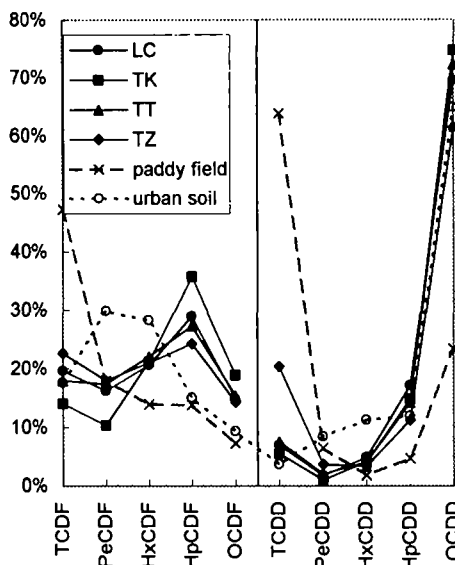


Figure 2 PCDD and PCDF profiles of sediment, paddy field and urban soil samples

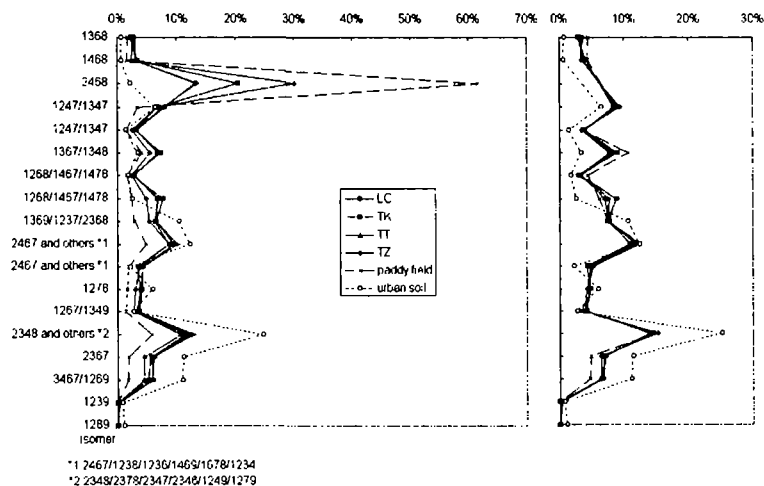


Figure 3-1 Isomer patterns of TCDF (left)

Figure 3-2 Isomer patterns of TCDF without 2,4,6,8-TCDF (right)

the herbicide CNP⁵). One of the main land uses in the Kasumigaura basin is as paddy fields, to which a large amount of CNP had been applied⁶). Therefore it is concluded that all sediment and paddy field samples were affected by PCDD/Fs originating from herbicide impurities. When 2,4,6,8-TCDF is removed from Figure 3-1, hypothetical TCDF patterns are obtained as shown in Figure 3-2, in which the isomer patterns of all the sediment and paddy field samples are very similar in contrast with urban soil sample. 1,3,6,8- and 1,3,7,9-TCDD are the main components of PCDD/Fs in CNP⁵) and these two isomers account for 98% of the TCDDs in paddy field sample and more than 90% of TCDDs in sediment samples. Hypothetical TCDD isomer patterns without 1,3,6,8- and 1,3,7,9-TCDD also show relatively similar patterns for all sediment and paddy field samples (not shown).

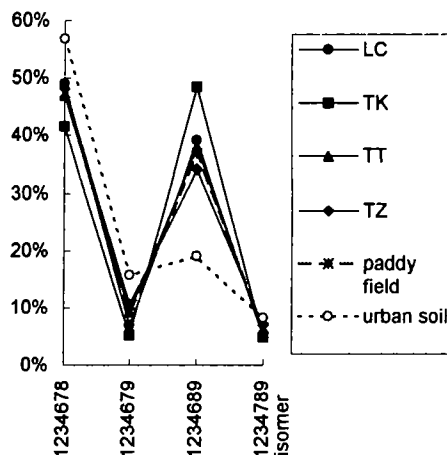


Figure 4 Isomer patterns of HpCDF

Figure 4 shows isomer patterns of HpCDF. Sediment and paddy field samples exhibit analogous patterns in which 1,2,3,4,6,7,8-HpCDF and 1,2,3,4,6,8,9-HpCDF are the two dominant isomers, while the urban soil sample shows a smaller contribution of 1,2,3,4,6,8,9-HpCDF. CNP is reported to contain a much lower concentration of higher chlorinated PCDD/Fs⁵) and is expected to have little influence on HpCDF patterns.

Isomer-specific determination and analysis were carried out for 4 sediment samples and one paddy field soil sample. Homologue profiles and isomer patterns of all sediment samples are generally in good accordance with each other. A paddy field herbicide is concluded to be one of the major sources of PCDD/Fs in Lake Kasumigaura sediment. Considerations on hypothetical TCDF and TCDD isomer patterns and similarity in HpCDF patterns suggest homogeneous source(s) of PCDD/Fs in sediments and paddy field soil, other than impurities in the herbicide CNP.

Financial support by Nippon Life Insurance Foundation is acknowledged.

REFERENCES

- 1) L. L. Lamparski and T. J. Nestrick, *Chemosphere*, **19**, 27-31, 1989
- 2) J. J. Ryan, H. B. S. Conacher, L. G. Panopio, B. P.-Y. Lau, J. A. Hardy and Y. Masuda, *J. Chromatogr.*, **541**, 131-183, 1991
- 3) U.S. EPA, *Method 1613*, 1990
- 4) Japanese Environment Agency, *Chemicals in the environment*, 229-242, 1994
- 5) T. Yamagishi, T. Miyazaki, K. Akiyama, M. Morita, J. Nakagawa, S. Horii and S. Kaneko, *Chemosphere*, **10**, 1137-1144, 1981
- 6) H. Ono and J. Nakanishi, *Wat. Res.*, **21**, 669-675, 1987