

# THE MONITORING OF DIOXINS AND RELATED COMPOUNDS IN RIVER WATER

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## Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs)/polychlorinated dibenzofuran (PCDFs) have 75 and 135 isomers of respectively. They are generated in the process of burning, breaching pulp and manufacturing pesticides. Polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs) have 209 and 75 isomers of respectively. PCBs and PCNs have been used widely and in large amount as heat medium, electrical oil and so on. It has been reported that PCBs and PCNs are also generated in the process of burning. These compounds are likely to Persist in environment due to their chemically and biologically stable natures. Therefore, bio-concentrations of these chemical compounds and their negative impacts on ecosystems have been pointed out. Some isomers of PCDDs, PCDFs, and PCBs are highly toxic and are suspected as endocrine disrupting substances. Moreover, the distributions of these isomers contribute to the collection of important information on their distributions, fates, and behaviors as well as released sources in environment. It is, therefore, important to monitor distributions and concentrations of these isomers in environment. In addition, since these chemical compounds have many isomers and persist at low concentrations in environment, these often cannot be detected in the water sample. To grasp these concentration levels and isomer distribution in the environment, river water must be collected in quantities in the sampling site.

Therefore, we collected river water 100L in the absorption using polyurethane form (PUF) in a sampling site and carried out the isomer specific determination of the dioxins by high resolution GC/MS-SIM (HRGC/HRMS-SIM). In this paper, results of this survey are presented.

## Materials and Methods

### *Sampling Methods*

Sampling has been done every other month in Kako River since July 1998. 100 L river water was transferred at about 2 L/min. to a glass container equipped with clean 5 polyurethane form (PUF: 8.5cm diameter x 5cm height). In this way, chemical compounds were adsorbed to each PUF and collected.

### *Sample Extraction and Cleanup*

PUFs were several extracted in acetone for 24 hours using Soxhlet extractors, and then extracts were reduced to 30mL and re-extraction with n-hexane. Extracts were purified by sulfuric acid, and then washed by water. Organic layer was dried on sodium sulfate, after concentrated to 1mL.

Clean up was carried out by a series connection of Sep-Pak silica and Carboxene1000R. The first fraction and the second fraction were combined and concentrated to 1mL for determination of PCBs without co-PCBs. The third fraction was concentrated to 0.1mL for determination of

PCDDs, PCDFs, co-PCBs, and PCNs.

#### ***GC/MS-SIM Conditions***

HRGC/HRMS-SIM analyses of Dioxins congeners were carried out on a JMS-700 mass spectrometer (JEOL) connected to a HP5890 gas chromatograph (Hewlett Packard). Gas chromatographic separation of samples was carried out on 25m fused silica capillary column of 0.2mmID, coated with a 0.33um film of 5% diphenyl polydimethylsiloxane (HP Ultra-2, Hewlett Packard). Helium was used as carrier gas at a linear velocity of 51.5cm/sec. An aliquot of 1uL of the sample was injected (using an all-glass falling needle injector). The injection port temperature was 250°C. The septum temperature was 250°C. The chamber temperature was 250°C. The HRGC was temperature programmed from 120°C(2min)-20°C/min-192°C(0min)-3°C/min-290°C(2min) for Te4-O8CDD/DF. The HRGC was temperature programmed from 70°C(2min)-8°C/min-300°C(8min) for M1-Tr3CDD/DF, PCB, and PCN. The mass spectrometer was operated in electron impact ionization mode with ionization energy of 47eV. The resolution was 10,000 (at m/z 331 of perfluorokerosene (PFK)). Quantification was carried out by isotope dilution mass spectrometry.

**Table 1. Concentrations of PCDDs, PCDFs, PCBs, and PCNs in river water samples.**

Conc. (pg/L)	Jul.1998	Sep.1998	Nov.1998	Average
PCDDs (4-8Cl)	110	72	11	63
PCDFs (4-8Cl)	4.0	1.9	0.1	2.0
PCDDs (1-3Cl)	89	66	54	70
PCDFs (1-3Cl)	13	14	15	14
PCBs	110	140	110	120
PCNs	23	30	22	25

#### **Results and Discussion**

Dioxins contained in 100L river water were adsorbed to polyurethane form (PUF) and collected for the analysis of isomers.

##### ***The concentrations of the dioxin and related compounds in river water samples***

Concentrations were shown in table 1. Concentrations of PCDDs/DFs (tetra~octa-chlorides) were lower a little in 11-110pg/L than in the literature value (1). PCDDs (mono~octa-chlorides) were 65-200pg/L (an average of 130) and PCDFs (mono~octa-chlorides) was 15-17pg/L (an average of 16). The concentrations of PCDDs/PCDFs decreased from July to November, but no changes in the concentrations of PCBs/PCNs were observed.

##### ***The homologue distribution of the dioxin and related compounds in river water samples***

Figure 1~4 show the homologue distribution. In dichlorinated dibenzo-*p*-dioxins, 2,6-/2,7-/2,8-D2DDs were predominated isomers. About 90% of tetra chlorinated dibenzo-*p*-dioxins was consisted by 1,3,6,8-T4CDD and 1,3,7,9-T4CDD. In tetra chlorinated dibenzofurans, 2,4,6,8-T4CDF, which had been originated from CNP, was the most important isomer. In dichlorinated biphenyls, four isomers, #11 (3,3'-), #15 (4,4'-), #12 (3,4-), and #13 (3,4'-)(IUPAC No.), were predominated isomers as seen to the atmosphere, the sediment and so on. Also, isomer of #35(3,3',4-), #37(3,4,4'-), #77(3,3',4,4'-), #126(3,3',4,4',5-), #156 (2,3,3',4,4',5-),

#157(2,3,3',4,4',5'-), #169(3,3',4,4',5,5'-), and #189(2,3,3',4,4',5,5'-), was detected.

Figure 5 shows the ratio of PCDDs and PCDFs. In atmospheric samples, the isomeric patterns of PCDDs and PCDFs resembled that of fly ash, however, in water and soil samples, the ratio of PCDFs had a tendency to decrease.

## References

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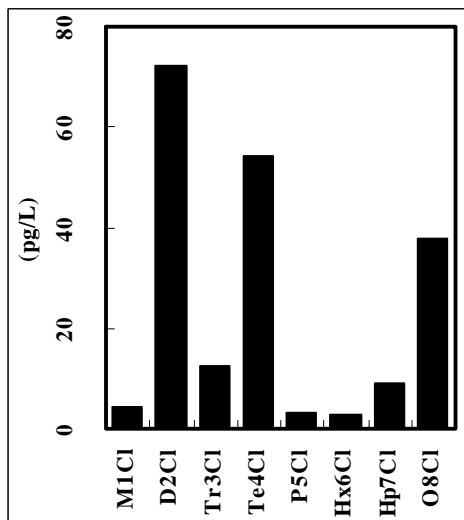


Figure 1. PCDD-profile in river water.

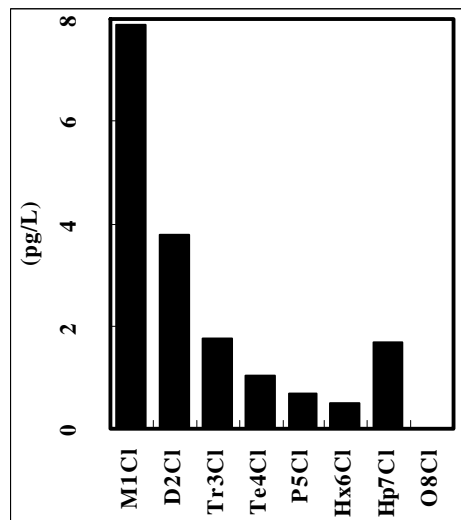


Figure 2. PCDF-profile in river water.

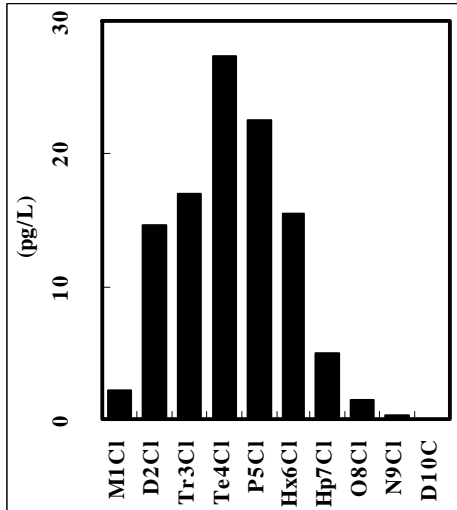


Figure 3. PCB-profile in river water.

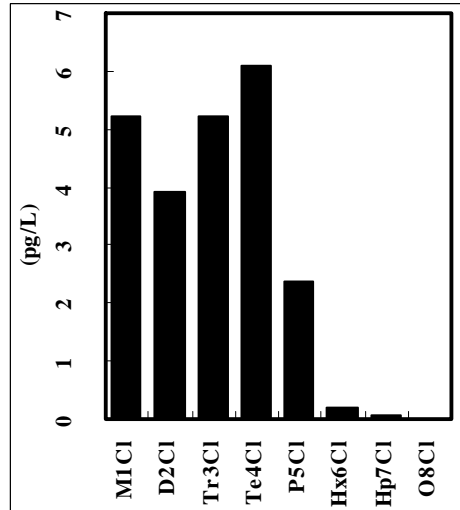


Figure 4. PCN-profile in river water.

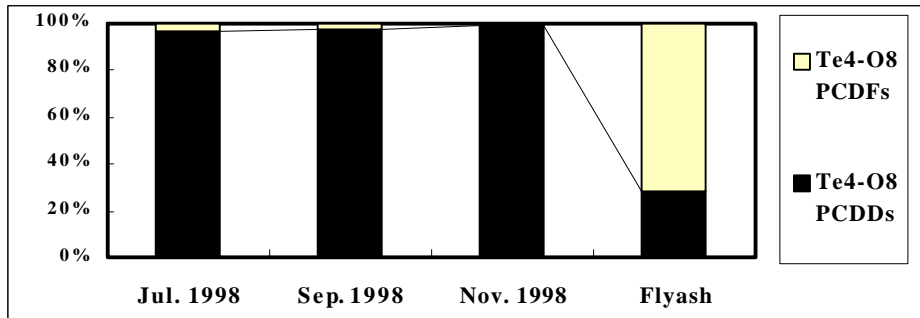


Figure 5-1. Comparison of Te4-O8CDDs and Te4-O8PCDFs in river water.

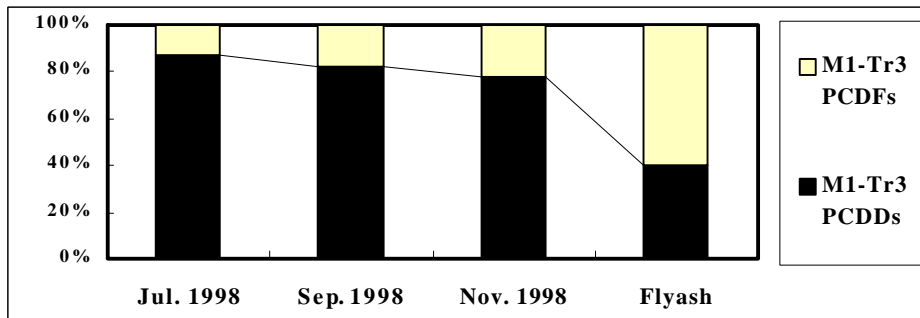


Figure 5-2. Comparison of M1-Tr3CDDs and M1-Tr3PCDFs in river water.