THE CONCENTRATION AND CHARACTERISTICS OF PCDDs/Fs IN SEDIMENT OF THE HAN-RIVER AND THE TRIBUTARIES

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Introduction

The Han river flows through in Seoul, Korea. There are three major tributaries which run into the Han river. The Han river has been used for agricultural, recreational, and domestic purpose as well as a source of potable water. They have been polluted by industrial and domestic waste water and the air containing heavy metal and organic contaminants such as dioxins for a long term. The concentration and characteristics of organic and inorganic components in the sediment of the Han river are well known, but that of PCDDs/Fs has not been investigated. In this study, characteristics of distribution and concentration of PCDDs/Fs in the sediment are researched and discussed.

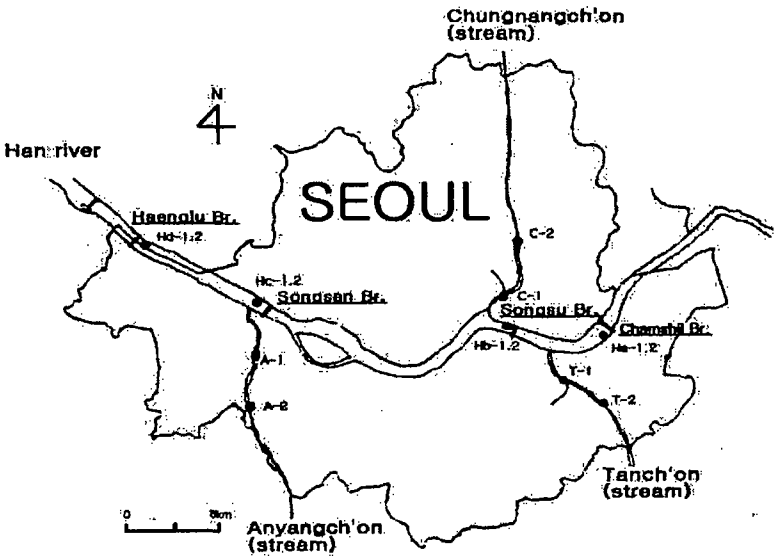

Fig 1. Sampling sites for the sediment in the Han river and its tributaries.

Method and Material

Sampling ; The fourteen sediment samples were collected from 10 sampling sites in the Han river and the tributaries(Fig.1) from January to March in 2000. The surface sediments(depth 0-10 cm) were collected with an Labostar bottom sampler. The samples are classified into two groups. The group-1(Xx-1) mainly consists of fine sand and coarse sand. The group-2(Xx-2) mostly comprises of silt and clay(Table. 1).

Table.1 Classification of samples

Group-1(Xx-1)		Group-2(Xx-2)	
No.	Sediment particle	No.	Sediment particle
Ha-1	Coarse sand and fine sand (>99%)	Ha-2	Silt and clay (>50%)
Hb-1	Coarse sand and fine sand(>95%)	Hb-2	Silt and clay (>99%)
Hc-1	Coarse sand and fine sand (>90%)	Hc-2	Silt and clay (>50%)
Hd-1	Coarse sand and fine sand (>90%)	Hd-2	Silt and clay (>80%)
T-1	Coarse sand and fine sand (>80%)	T-2	Silt and clay (>70%)
A-1	Coarse sand and fine sand (>80%)	A-2	Silt and clay (>70%)
C-1	Coarse sand and fine sand (>80%)	C-2	Silt and clay (>70%)

Analytical Procedure: The samples were dried in a stainless box for a few days. The dried samples were crushed with a steel blender and sieved, only the fraction <2 mm was analyzed[1]. Each sieved sample(20g) was spiked with fifteen 2,3,7,8-substitued $^{13}C_{12}$-labeled PCDDs/Fs as internal standard (100pg/μl × 20μl), and then extracted with 350ml of toluene by soxhlet extractor at the rate 4 times/hour during 18hr[1]. The toluene extract was concentrated to nearly dryness and dissolved in 150ml of n-hexane. The n-hexane layer was treated with conc. sulfuric acid(10ml) in a separate funnel until remaining color was removed completely, and then washed with distilled water(100ml) 2 times. This step was followed by a purification in a multi-layer silica column with n-hexane and alumina column with dichloromethane/n-hexane(50:50). The purified extract was concentrated to final volume 20μl under nitrogen stream, and then spiked with $^{13}C_{12}$-labelled 1,2,3,4- and 1,2,3,7,8,9-substitued PCDDs as recovery standard. The extract was analyzed by HRGC-HRMS on Micromass VG Autospec Ultima epuipped with a CE 8000 series gas chromatograph, operating at 10,000 resolving power in the SIM mode, using a 60m DB-5ms fused silica capillary column(0.32mm id × 0.25μm film thickness).

Result and Discussion

The total concentration of PCDDs/Fs in the all sediments ranged from 3.93 to 245.2 pg/g dry weight, and TEQ values of them ranged from 0.04 to 4.39 pg-TEQ/g. The mean value of total concentration in Group-1(Xx-1 or X-1) was 7.693 pg/g d.w. and the average of TEQ values was 0.159 pg-TEQ/g, and those of group-2 were 104.708 pg/g d.w. and 1.976 pg-TEQ/g, respectively. The TEQ values of PCDDs/Fs in sediment from 12 rivers in Japan ranged from<0.02 to 24 pg-TEQ/g, reported by Japan Environment Agency (1995)[4]. Japan which is adjacent to Korea operates waste incinerator more than Korea, so more or less value of PCDDs/Fs is high.

Possibly the big disparity between group-1 and group-2 is due to characteristic of the sediment, not site. Total concentration and TEQ values of the Xx-2 samples were much higher than those of Xx-1(Fig.2).

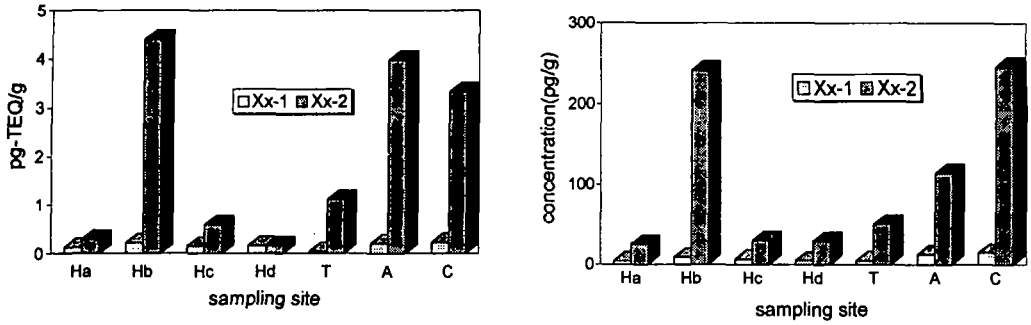

Fig 2. Total PCDDs/Fs and TEQ values in sediment.

The Xx-2 samples have silt and clay much more than Xx-1(Table.1). Especially sample of Hb-2 was mud sediment nearly 100%, thus get so great liquidity and very high water capacity, which may cause Hb-1 to be different from Hb-2 by about 20 times, regardless of almost same sampling site. There was disparity of characteristic in sediment but rare difference of TEQ values between sample Hd-1 and Hd-2. A-1 is located in downstream of Kuro factory district, A-2 is located on the upper. Both of A-1 and A-2 site have offensive odor. Especially sample A-1 was black and polluted by waste water too much, and sample A-2 has much more clay and mud than A-1 only. Total concentration and TEQ value of sample A-1 was less much than those of A-2. It is said that the sediment is scarcely influenced by waste water discharged from the factory district.

Characteristics of distribution of PCDDs/Fs isomers is shown Fig. 3. Regardless of the big difference of the total concentration, the relative abundance of each isomer show almost same figure. The sample A-2 was a little bit different. The value of 1,2,3,4,6,7,8-HpCDF in A-2 was high comparatively.

The percentage of OCDD in whole PCDDs/Fs ranged from 21% to 72% and the average was 55%, and that of OCDF ranged from 6.5% to 17.5% and the average was 12.0%. The proportion of the octa-CDs/Fs in total concentration reached to 77%. There was a noteworthy distribution-characteristic, which the value of 1,2,3,4,6,7,8-HpCDF was much higher than 1,2,3,4,7,8,9-HpCDF. The percentage of PCDFs in total concentration ranged from 18% to 68% and PCDDs ranged from 31% to 82%. The mean of PCDFs is 34% and PCDDs is 66%. The relative abundance of PCDDs doubled that of PCDFs nearly. The higher chlorinated dioxins, the lower solubility in water and the higher octanol/water partition[2]. It makes octa-and hepta-CDs/Fs remain longer than the other isomers in environment. There is hardly major water pollution source for dioxins close to the Han river. Supposedly the level of PCDDs/Fs in the Han river was originated in atmospheric deposition[2]. The pattern of PCDDs/Fs discharged from big waste incinerator was different from that of sediment in Seoul last year. The percentage of octa-CDs/Fs in total concentration of the released gas was about 42% and the other isomers were distributed more even than that of sediment sample. After released from the chimney, the dioxins were degraded by photolysis and hydroxylation in the air and change to low toxic matter slowly in sediment[2].

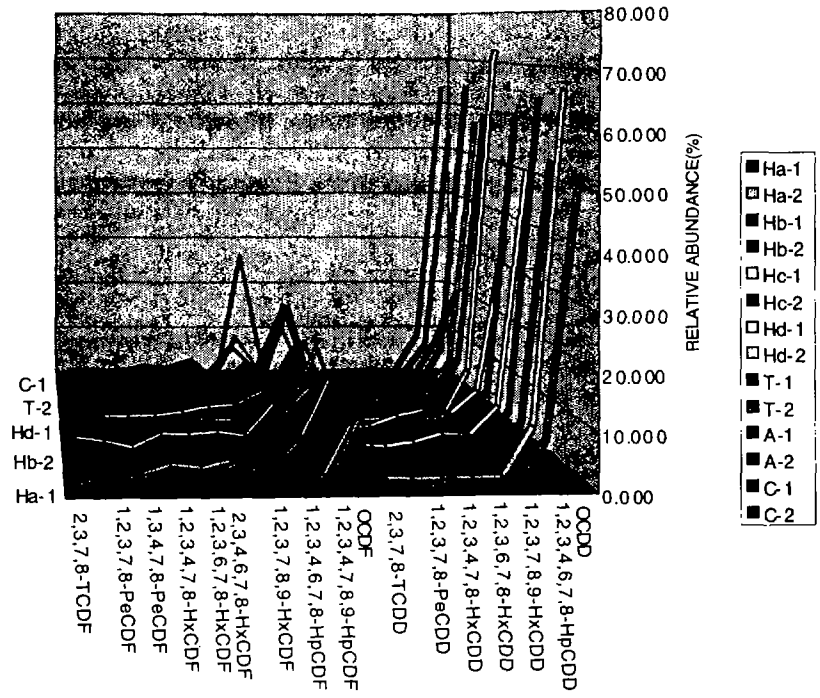

Fig. 3. Relative abundance of PCDDs/Fs in sediment.

References

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