POLYCHLORINATED BIPHENYLS IN SEDIMENTS OF THE KUMHO RIVER IN S. KOREA

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Introduction

The Kumho River is one of the major tributaries of the Nakdong River located southeastern region in Korea. The objectives of this study are to investigate the distribution levels of PCB congeners in sediments of the Kumho River and to estimate the effect of the Kumho River on the contamination level of the Nakdong River. Sediments were collected using a grab sampler at 23 sites along the river in September 1999. PCBs were extracted by liquid-liquid extraction and cleaned by using adsorption chromatographic techniques and concentrated sulfuric acid. A HP6890 gas chromatograph equipped with an electron capture detector was used for quantification. The total PCB level is ranged from 2.7 to 87.6 ng/g dry weight. The levels of PCB congeners are significantly correlated with the total organic carbons in sediments. The major fractions of PCBs are congeners containing 4, 5, and 6 chlorine atoms per biphenyl molecule.

Methods and Materials

Sampling was done at 23 sites along the main stream and tributaries of Kumho River, with a grab sampler in September 1999. Sampling sites are illustrated in Fig. 1. The sampling points were selected at the center part of the river. Sediments were freeze dried, treated with a 2 mm standard molecular sieve, and stored in a -4℃ refrigerator by sealing into the polyethylene bottle before analysis. The individual 26 PCB congeners were used as the standard reference substances and 1-chloronaphthalene was used as an internal standard. The reference soil SRM 1939a (NIST U.S.A.) was applied for the recovery test. The average recovery rates are ranged from 81.6% to 110.8%. These recovery rates were acceptable, so we did not correct the experimental results. N-hexane and acetone were used as the solvents for extraction and cleaning glassware. Anhydrous sodium sulfate was dried for 4 hours at 130℃ and used to remove trace levels of water in the extracts. Sulfuric acid was used to remove the interfering substances. Silica gel and florisil were stored in the oven just before cleaning up after activating for 9 hours at 130℃ and applied in the cleanup process. Standard solutions and final samples were determined with a gas chromatograph (Hewlett Packard 6890 series, U.S.A.) with a ^{63}Ni electron capture detector and an automatic sampler. A HP-5 (5% diphenyldimethylsiloxane, Hewlett-Packard) capillary column with an 0.32 mm inner diameter, 30 m length, and 0.25 ㎛ film thickness was used as a separation column.

Walkley-Black's wet oxidation method was applied to determine the total organic carbon content (TOC) in sediments to investigate the correlation between the contents of organic carbon and PCBs. The detailed process was described in the previous work[1].

Results and Discussion

The variation trend of the total PCB levels along the main stream Kumho River is illustrated in Fig. 2. The total PCB levels for the 26 congeners ranged from 2.7 to 87.6 ng/g as shown in Table 1. The highest level was obtained from site-18 near Keomdan factory district, and the nearby site-17 also showed 57.5 ng/g as the fourth highest level. The second and third highest levels were also located near west Daegu factory district (site-5) and the 3rd factory district (site-10), respectively. These results imply that PCB level is highly dependent on the location of factory district at which various organic pollutants may be discharged. PCBs showed, in another work, highest concentrations in sediments taken from locations close to the industrial area[2]. The effect of point sources on the total PCB levels are definitely illustrated in Fig. 2 at which total PCB levels are dramatically increased near factory districts, site-18, 10, 5. These levels, however, are much lower than the limit level 10,000 ng/g over which river sediment should be dredged in Japan[3]. By comparing wih our previous work[1] of the lower Nakdong River, sediments from the Kumho River showed much higher level and more even distribution. In the lower Nakdong River, the average level was only 3.8±2.6 ng/g excluding the highest three sites. In the Kumho River, however, the average level is 26.3±23.9 ng/g, which is about 7 times higher than the average level of the lower Nakdong River.

The five sites (site-1, 15, 16, 19, 23) which showed lowest level of 2.7~7.0 ng/g are all located at the upper (site-15, 16, 19) stream of the Kumho River and at the main stream of the Nakdong River before and after confluence of these two rivers (site-1, 23). The three sites (site-15, 16, 19) showed PCB levels from 2.9 to 5.9 ng/g, which indicate the upper stream from these sites of the Kumho River is not contaminated. There are actually no point contamination sources beyond these sites. The main stream Nakdong River at site-23 showed much lower level of PCBs (4.9 ng/g) compared with the main stream Kumho River (average level is 27.2 ng/g). These observations indicate that any specific point sources exert a great influence on the PCB level in sediments and most PCBs are deposited into nearby sediments. These results also imply that only a small proportion of PCBs is transported through water stream. We observed no apparent direct effect of the Kumho River on the PCB level of the Nakdong River. The influence, however, may continue for a long time period via exchange process of PCBs between sediments and water layer.

The total TEQ value listed in Table 1 was calculated based on the TEF values of World Health Organization (WHO). The total TEQ value is 1,036 pg TEQ/g dry weight, and that from PCB 126 is 993 pg TEQ/g dw. This means PCB 126 whose WHO-TEF value is 0.1 contributes 96.0%

of the total TEQ although this congener occupies only 1.6% of the total PCB level. For each sampling site, contribution of PCB 126 to the total TEQ value ranges from 90.6% to 99.7% with average value 96.0%. The correlation coefficient, *r*, between the total TEQ value and the concentration of PCB 126 is 1.00. Thus, if the value of total TEQ in sediments of this river is concerned, it is sufficient to determine only one specific congener PCB 126. The *r* of between the total TEQ value and the total PCB level of 23 congeners is 0.782. Among 23 sampling sites, the four sites (site-10, 13, 17, 18) contributes 48.5% of the total TEQ value with average of 125 pg TEQ/g d.w.. These four sites are all located along the main stream of the Kumho River and affected from the factory districts. The average TEQ value of the other 13 sites is 41 pg TEQ/g d.w., and PCB 126 was not detected from the other five sites.

The content of TOC is depicted in Table 1. The site-18, where the highest total PCB level was observed also showed the highest content of organic carbons. The sites 16 and 19 showed the lowest content of TOC, at which total PCB also showed the lowest level. We found a general trend that total PCB levels increase as the TOC content increases. The correlation coefficient of these two parameters is 0.84, which indicates significant correlation between them.

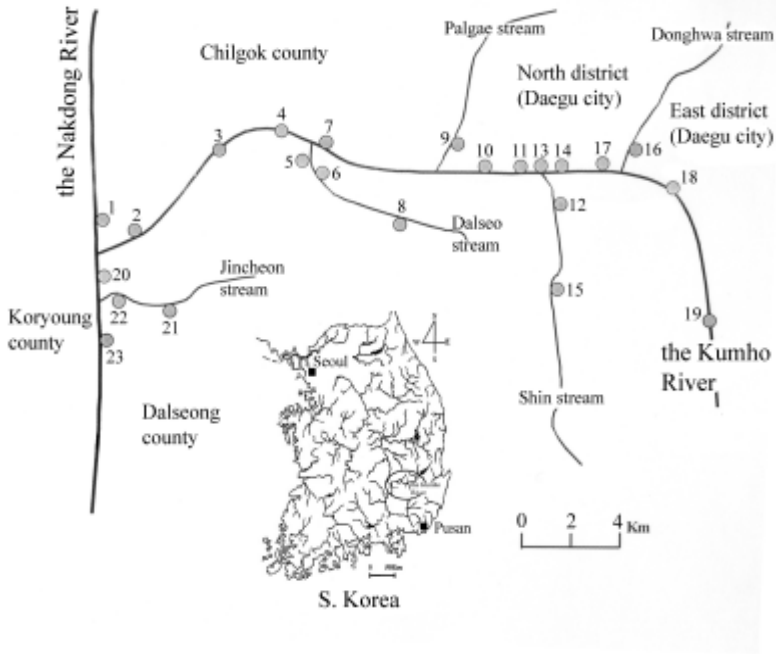

Fig. 1. Sampling sites along the Kumho River, Korea

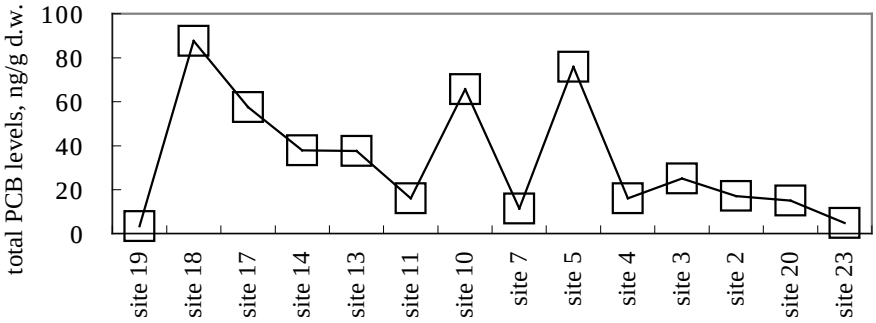

Fig. 2 The variation trend of total PCBs along the main stream Kumho River

Table 1. Total concentrations for 26 PCB congeners, TEQ values and the content of total organic carbon in sediments from the the Kumho River.

Site No.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Total PCBs, ng/g	7.0	17.2	25.1	16.1	75.8	13.4	11.4	26.3	33.2	65.7	16.1	32.4
pg TEQ/g	19.2	66.3	26.2	28.8	82.3	14.6	21.1	48.5	44.1	127	0.54	66.8
Average TOC, %	2.25	4.42	3.95	3.47	5.38	2.98	2.50	4.43	4.42	4.90	3.69	4.42
Site No.	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	
Total PCBs, ng/g	37.6	37.8	5.9	2.7	57.5	87.6	3.4	15.1	30.0	8.0	4.9	
pg TEQ/g	123	0.64	22.1	4.92	147	105	0.07	42.4	44.8	0.50	0.07	
Average TOC, %	4.43	4.66	1.29	1.07	5.13	5.86	1.06	3.22	4.18	3.47	1.78	

References

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