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# Source Identification and Concentration Distribution of Polychlorinated Biphenyls (PCBs) in River Sediment

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***Abstract*—In order to grasp the concentration distribution and to identify sources for PCBs of Nakdong-river, surficial sediment samples were collected and whole 209 congeners were analyzed. And Principal Component Analysis (PCA) was carried out for source identification. The level of total PCBs in sediment samples was ranged from 124.43 to 79,241pg/g-dry. And the concentration of coplanar PCBs was 17.662 to 6,550.4 pg/g-dry (0.000 ~ 2.908 pg WHO-TEQ/g-dry). In terms of homologue composition, higher portion of high-chlorinated biphenyls (hexa- to hepta-CBs) was shown in samples with higher concentration of PCBs. And isomer composition of each homologue was so much similar from sample to sample and it was prominent in high-chlorinated biphenyls (hexa- to octa-CBs). Among the whole 209 congeners of PCBs, 25 congeners were selected for PCA based on the detection magnitude in sediment samples and representativeness for each source. According to the result of PCA, sediment of Nakdong-river was mainly affected by Aroclor products (1242, 1254 and 1260). The portion of incineration and Aroclor 1248 was regarded to be relatively insignificant.**

***Keywords – Polychlorinated Biphenyls; Principal Component Analysis; Sediment; Source Identificiation***

## I. INTRODUCTION

Polychlorinated Biphenyls (PCBs) are one of Persistent Organic Pollutants (POPs). It had various applications, for example, mainly as dielectric fluids in transformers and capacitors, as plasticizers, and carbonless copying paper due to its outstanding physical and chemical properties [1]. But, its production and usage was prohibited since the adverse effect to human health and ecosystem was reported.

In Korea, PCBs are being classified as specified waste. In particular, transformer oils (as liquid waste) have been of great concern nowadays because of its large amount. Though Korea isn't a country had produced PCBs, PCBs is still being detected in environmental matrices. National Institute of Environmental Research (NIER) has been carrying out nationwide survey annually on level of Endocrine Disruption Compounds (EDCs) including PCBs [2]. The survey has been being conducted on various environmental matrices, but seldom on sediment though it is regarded to be final destination as well as source of environmental pollutants to hydrospheric system.

Nakdong-river is the second largest river in Korea. Its pollution problem has been a matter of great concern from earlier because there are various industrial facilities alongside of the river. Also, since it supplies huge amount of water for agricultural, industrial and residential purpose and many kinds of livings exist in the river, its role to south-eastern part of Korea is so much crucial.

Therefore, surficial sediment samples were collected from Nakdong-river and the whole (209) congeners were analyzed. And the concentration distribution and source identification of PCBs were examined in this study.

## II. MATERIALS AND METHODS

### *A. Sampling and Analysis*

Sampling was performed from May to June 2006. Totally, 21 sampling points were selected and 3 duplicate samples were collected by each point. Sampling points of this study was shown in Fig. 1. The extraction of samples was performed by soxhlet extractor for more than 16 hours with toluene. Prior to extraction, cleanup standard (EC-4977, Cambridge Isotope Laboratories Co.) was injected. Extracts were completely changed to n-hexane and sulfuric acid treatment was carried out. Then, multilayer column cleanup was carried out and absorbents were as follows from the bottom; neutral silica-gel (activated at 130℃ for more than 19 hours) 1g, 30% potassium hydroxide coated silica-gel 2g, neutral silica-gel (activated at 130℃for more than 19 hours) 1g, 44% sulfuric acid coated silica-gel 4g, neutral silica-gel (activated at 130℃for more than 19 hours) 1g, 10% silver nitrate coated silica-gel 1g, anhydrous sodium sulfate 2g.

Then, copper column was carried out to remove sulfur easily contained in anaerobic condition and alumina column (activated at 190℃ for more than 19 hours, 14g) was carried out finally. Prior to elusion, alumina column was cleaned by 50mL of n-hexane and pre-fraction (90mL of n-hexane) was discarded. And the post-fraction (30mL of 50% dichloromethane/n-hexane) was used for instrumental analysis. After injecting syringe standard (EC-4979, Cambridge Isotope Laboratories Co.), high resolution gas chromatography / high resolution mass spectroscopy (HRGC/HRMS) analysis was carried out. HRGC/HRMS analysis was performed in the EI-SIM (Electron Impact / Selected Ion Monitoring) mode, with a resolution of more than 10,000. The capillary column was DB-5MS capillary column (60 m × 0.25 mm × 0.25 μm, J&W Scientific). All reagents and organic solvents used were of PCB-analysis grade or pesticide analysis grade and the detailed procedure on pre-treatment was based on [3].

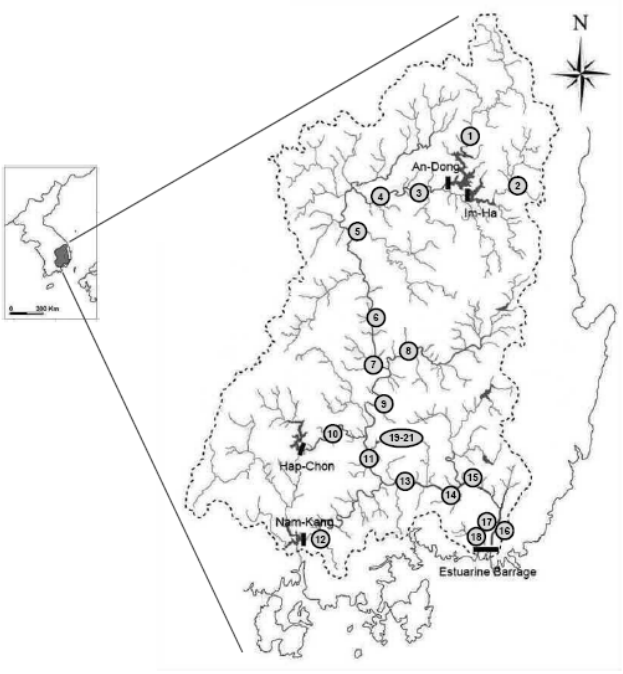


Figure 1. .Sampling points around Nakdong-river

## B. Principal Component Analysis (PCA)

The basic assumption for receptor models is that the concentration of a pollutant at a receptor for a given sample is the linear sum of the products of the emission profile and contribution of sources. And samples are well mixed with chemicals from different sources and the chemicals are relatively stable during the transport from the emission source to the receptor site. Among many statistical methods, PCA is the most representative method for source identification. In order for the easiness of interpretation, it reduces the number of variables while retaining the original information as much as possible. The detailed procedure of PCA was shown in previous papers [4, 5].

# III. Results and Discussion

## A. Concentration distribution of PCBs

The PCBs level of relatively wide range was obtained. The concentration of total PCBs in Nakdong-river's surficial sediments was ranged from 124.43 to 79,241pg/g-dry. Also, the concentration of coplanar-PCBs (12 congeners; #81, #77, #123, #118, #114, #105, #126, #167, #156, #157, #169, #189) was ranged from 17.662 to 6,550.4 pg/g-dry (0.000 ~ 2.908 pg WHO-TEQ/g-dry). Since Toxic Equivalent Factor (TEF) of coplanar PCBs is much lower than polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs), TEQ level of some samples was close to zero. In homologue composition, tri- ~ hexa-chlorinated biphenyls (3~6CBs) were predominant. The higher total PCBs concentration was, the higher portion of high-chlorinated biphenyls (6~7CBs) was. In terms of isomer composition of each homologue, almost all samples were so much similar to each other, which had been reported by [6]. In particular, it was more prominent in high-chlorinated biphenyls (6~8CBs). Similar aspect was reported by previous paper on soil around industrial complex [7]. Generally, the level of upstream region was lower than the midstream and downstream. The coplanar PCBs level of each sediment sample was shown in Fig. 2.

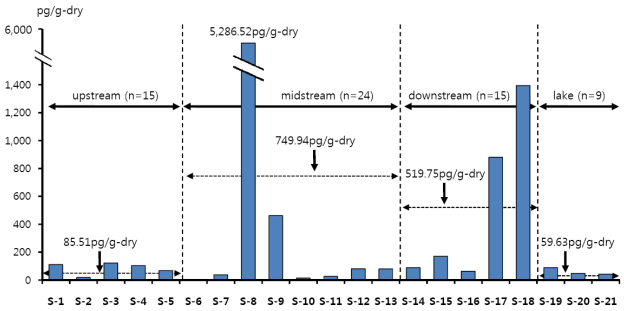


Figure 2. The concentration of coplanar PCBs in this study

Some samples (S-8, 9, 17, 18) have shown relatively high concentration of coplanar PCBs. Around these sampling points, more facilities were congregated than others. In particular, about 20% of the total landfill leachate treatment facilities were located around S-8.

## B. Source identification

The data matrix (congeners by samples) should be arranged prior to carry out PCA. It is very useful to identify and apportion each source with whole congeners of PCBs, but 209 congeners are too many for PCA compared to number of samples in this study. Also, it can make interpretation of result a little bit complicated if whole 209 congeners would be used for PCA. Therefore, 25 congeners (#10&4, #9&7, #14, #11, #12&13, #15, #17, #72&71, #84, #97&86, #85&120, #151, #135&144, #141, #128, #179,

#182&187, #183, #174&181, #177, #180&193, #170&190, #199, #203&196, #194) which tended to be highly detected in sediment samples were selected. And it was also checked whether they were relatively predominant congeners in source composition (Aroclor 1242, 1248, 1254, 1260 and Incineration) or not. The composition profiles of Aroclors were obtained from U.S. Environmental Protection Agency (EPA) and incineration composition was obtained from [8].

Prior to perform PCA, the composition profile with selected 25 congeners was prepared for each source (see Fig. 3). This procedure can help interpreting the result of PCA (designating extracted factor as a source or mixed sources) and judging whether or not each source's composition with selected congeners represents the original characteristic. As shown Fig. 3, low-chlorinated congeners such as #10&4, #9&7, #14, #11, #12&13 had relatively higher portion in incineration and Aroclor 1242. Also, Aroclor 1260 had higher portion of most high-chlorinated biphenyls. In case of Aroclor 1248, only #72&71 was predominant compared to other sources.

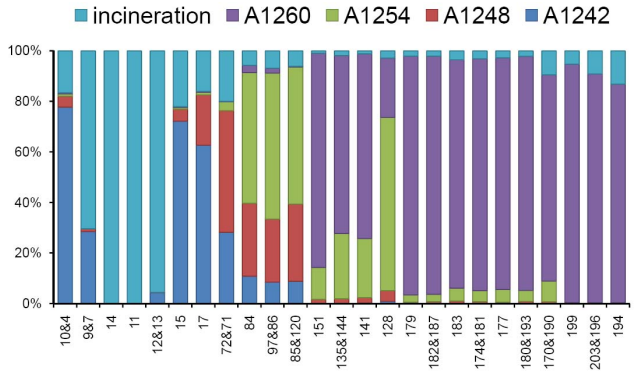


Figure 3. Comparison of each source's composition profile

PCA was carried out by using SPSS 12.0 and VARIMAX, which is the most commonly used orthogonal rotation method, was performed for easiness of interpretation of each factor extracted by PCA. Totally, 3 factors (96.04% of cumulative variance) of which eigenvalue were more than 1.0 were extracted and the factor loadings were shown in Fig. 4.

Based on the composition profile of Fig. 4, Aroclor 1254 and 1260's congeners were positively correlated with factor 1 (61.87% variance of the total). On the other hand, Aroclor 1242 and incineration were highly positive-correlated with factor 2 (28.53% variance of the total). Among 3 factors, the factor that #72&71 was positive-correlated with was only factor 3 (5.66% variance of the total). According to the result of PCA, PCBs in Nakdong-river's sediment was mainly originated from Aroclor products. Even though incineration couldn't be separated from Aroclor 1242, it is anticipated not to affect total PCBs concentration in Nakdong-river's sediments seriously.

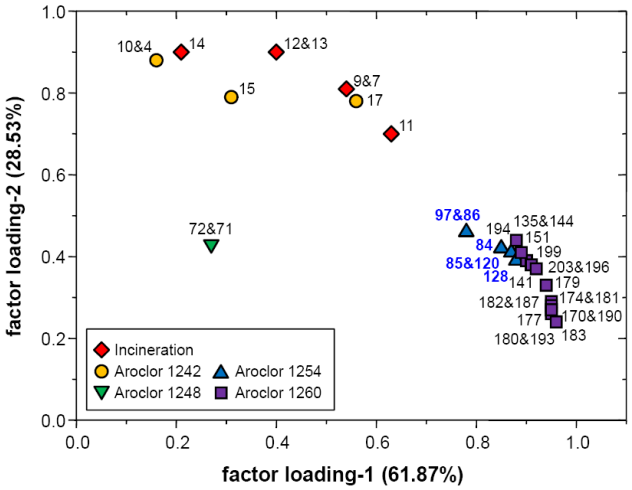


Figure 4. Factor loadings of PCA (VARIMAX rotated)

Similar result on soil samples around industrial complex has been reported [7]. The portion of each Aroclor product wasn't separated from each other, but the portion of incineration was insignificant compared to Aroclors. Normally, soil and sediment were regarded to be a final destination of pollutants. Therefore, it is regarded they tend to contain high-chlorinated biphenyls easily. Aroclor 1248 has been used as qualification standard in Waste Official Test Method (WOTM) of Korea. However, it has never been detected yet from sample and the portion of Aroclor 1248 in this study was also insignificant.

## IV. Conclusion

Nakdong-river is the second largest river in Korea and has been regarded to be important to south-eastern part of Korea. The pollution problem of Nakdong-river has been of great concern, so surficial sediment samples were collected and whole 209 congeners were analyzed in order to examine the concentration distribution of PCBs and source identification. Generally, the PCBs level of upstream region was lower than the midstream and downstream. In case of some samples from sample points that landfill leachate treatment facilities were densely located, level of PCBs was much higher than other samples.

Compared to the number of sediment samples, 209 congeners of PCBs were too many to perform PCA. Thus, 25 congeners were selected by considering magnitude and frequency of detection in sediment samples and source composition. According to the result of PCA, Nakdong-river's sediments were mainly affected by Aroclor 1254 and 1260. Incineration source wasn't separated from Aroclor 1242 and the portion of Aroclor 1248 was insignificant. This was to some extent similar result with previous paper that has investigated on soil around industrial complex.

There are various kinds of kind receptor models and they were complementary to each other. Thus, it is expected to be meaningful to compare with other models' result for more reasonable result.

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