# DISCHARGE CHARACTERISTICS OF COPLANAR PCBS FROM WASTEWATER DISCHARGE FACILITIES

Kim Sam-Cwan, Park Sun-Ku, Kim Kum-Hee, Hwang Seung-Ryul, Kwon Myung-Hee, Lee Jung-Hee, Choi Jong-Woo, Hong Suk-Young, Kim Chang-Hoe, Kim Dong-Hoon

National Institute of Environmental Research, Environmental Research Complex, Kyungseo-Dong, Seo-Ku, Inchon, 404-708, Republic of Korea

**Abstract**

In this study a total of 7 wastewater treatment facilities have been selected to investigate discharge characteristics of 12 coplanar PCBs known as dioxin-like toxicity by WHO and sampling was performed on influent, effluent and sludge. Each sample analyzed with HRGC/HRMS followed by multilayered silicagel column cleanup. The concentration of coplanar PCBs was at the range of 0.153 ~ 10.012 ng/L (0.020 ~ 13.807 pg WHO-TEQ/L) in influent, 0.011 ~ 0.785 ng/L (0.001 ~ 0.269 ng WHO-TEQ/L) in effluent and 0.199 ~ 21.341 ng/g dry weight (0.021 ~ 11.098 pg WHO-TEQ/g dry weight) in sludge samples and the removal efficiency in studied wasterwater treatment facillities was 55.8 ~ 99.9 %. Characteristics of congeners distribution were as follows ; 3,4,4',5-TetraCB (#81) and 2,3',4,4',5-PentaCB (#118) were highly detected in pulp, 2,3,4,4',5-PentaCB (#114) and 2,3,3',4,4',5-HexaCB (#156) in paper, 2',3,4,4',5-PentaCB (#123) and 2,3,3',4,4',5'-HexaCB (#157) in pesticide manufacture, 3,3',4,4',5-PentaCB (#126) and 3,3',4,4',5,5'-HexaCB (#169) in MSWI respectively.

**Introduction**

Although the production and use of polychlorinated biphenyls (PCBs) have been prohibited in most countries, PCBs still exist in environment and pose potential risk of chronic eco-toxicity due to their accumulating properties in soil and organism.[1] Of the 209 PCBs congeners, the twelve coplanar PCBs congeners (non-ortho PCBs 77, 81, 126, 169 and mono-ortho PCBs 105, 114, 118, 123, 156, 157, 167, 189) have been identified as producing dioxin-like toxicity due to the quasi-planar configuration.[2] So, they have been assigned toxic equivalency factors (TEF) by the World Health Organization (WHO)[3], and great concerns have been paid on them in recent years.

Toxic substances can enter surface water from a variety of discharge sources, including domestic and industrial wastewater treatment plants (WWTPs).[1,4] Accordingly, wastewater discharge facilities are widely recognized as a major source of toxic contaminants to aquatic environment, and controlling their effluents is thought to be essential.[4,5] The detection of trace level of coplanar PCBs have been reported in most of sewage sludges, raw wastewaters and effluents. However, coplanar PCBs data from wastewater discharge facilities are not much in comparison with those from air emission facilities. Therefore, this study was performed to investigate the discharge status and congener profiles on 12 kinds of coplanar PCBs in influent (raw wastewater), effluent and sludge from major wastewater discharge facilities.

**Materials and Method**

A total of 7 wastewater treatment plants were selected from sewage treatment plants, manufacturing facilities, including pulp, paper, chemicals and pesticides, and municipal solid waste incinerator (MSWI) equipped with wet scrubber. Influent, effluent and sludge were sampled from target discharge facilities, respectively, and scrubbing water was collected from wet scrubber of MSWI in 2005.

Raw wastewater and scrubbing water were divided into two phases through the filtration by the glass fiber filter of 0.9μm pore size: liquid phase (filtrate) and solid phase (suspended solid, SS). SS (filter pads) and sludges were air-dried, and manually ground before extraction. Filtrates and effluents were extracted twice with pesticide-grade dichloromethane. Sludges and filter pads were Soxhlet-extracted for 16 hours with dichloromethane. After extraction, crude extracts were treated with concentrated $H_2SO_4$, and cleaned up through multi-layer silica gel column ($Na_2SO_4$ 6g, 10% $AgNO_3$ silica gel 3g, silica gel 0.9g, 22% $H_2SO_4$ silica gel 3g, silica gel 0.9g, 44% $H_2SO_4$ silica gel 3g, silica gel 0.9g, 2% KOH silica gel 3g, silica gel 0.9g), followed by alumina column and activated carbon column. If impurities were not removed by these column-cleanup procedures mentioned above, fractionation was accomplished by HPLC with $C_{18}$ column. After cleanup, eluants were concentrated to a volume of 50 μl and quantified by high-resolution gas chromatography/high-resolution mass spectrometry (Agillant 6890/ Autospec Ultima, Micromass Co.) above 10,000 resolution with a DB-5MS column (60 m × 0.32 mm inner diameter × 0.25 μm). Toxic equivalents as 2,3,7,8-TeCDD (TEQs) were calculated by using the WHO-TEF for 12 kinds of coplanar PCBs. The method detection limit was 2 pg/L (S/N = 5:1), and recoveries of $^{13}C$-PCBs were in the range of 57 ~ 119 %.

**Results and Discussion**

As shown in Table 1, 0.153 ~ 10.012 ng/L (0.020 ~ 13.807 pg WHO-TEQ/L) of coplanar PCBs were contained in raw wastewaters, 0.011 ~ 0.785 ng/L (0.001 ~ 0.269 ng WHO-TEQ/L), in effluents, and 0.199 ~ 21.341 ng/g dry weight (0.021 ~ 11.098 pg WHO-TEQ/g dry weight), in sludges of wastewater discharge facilities.

The concentrations of coplanar PCBs in filtrate and SS of raw wastewaters were in the range of 2.7 ~ 81.9 % and 18.1 ~ 97.3 %, respectively. In particular, coplanar PCBs were mostly contained in SS, and their removal percents in WWTPs investigated were in the range of 55.8 ~ 99.9 %.

Byrns[6] predicted that adsorption on SS is the major removal mechanism for organic compounds in wastewater with a log $K_{ow}$ higher than around 4.5. As coplanar PCBs are hydrophobic contaminants[7] with a log $K_{ow}$ more

Table 1. Concentrations and removal efficiencies of coplanar PCBs in wastewater treatment facilities

| Facilities | Influent (Raw wastewaters) | | | | Effluent | | Sludge | | RE |
|---|---|---|---|---|---|---|---|---|---|
| | Filtrate | SS | Total | | | | | | |
| | ng/L (%) | ng/L (%) | ng/L | pg WHO-TEQ/L | ng/L | pg WHO-TEQ/L | ng/g d.w.[4)] | pg WHO-TEQ/g d.w.[4)] | (%)[5)] |
| WWTP-1[1)] | 0.086 (39.0) | 0.134 (61.0) | 0.220 | 1.349 | 0.018 | 0.067 | 13.681 | 2.140 | 91.8 |
| WWTP-2[2)] | 0.069 (6.1) | 1.066 (93.9) | 1.135 | 0.772 | 0.020 | 0.269 | 21.341 | 8.521 | 98.2 |
| Pulp | 0.127 (81.9) | 0.028 (18.1) | 0.155 | 0.020 | 0.017 | 0.002 | 0.199 | 0.021 | 89.1 |
| Paper | 0.340 (3.4) | 9.672 (96.6) | 10.012 | 3.915 | 0.013 | 0.001 | 8.271 | 1.779 | 99.9 |
| Chemical | 0.048 (31.4) | 0.105 (68.6) | 0.153 | 0.358 | 0.023 | 0.248 | 4.381 | 11.098 | 85.0 |
| Pesticide | 0.013 (2.7) | 0.838 (97.3) | 0.851 | 1.028 | 0.785 | 0.175 | 0.576 | 0.176 | 55.8 |
| MSWI[3)] | 0.042 (5.4) | 0.736 (94.6) | 0.778 | 13.807 | 0.011 | 0.121 | - | - | 98.6 |

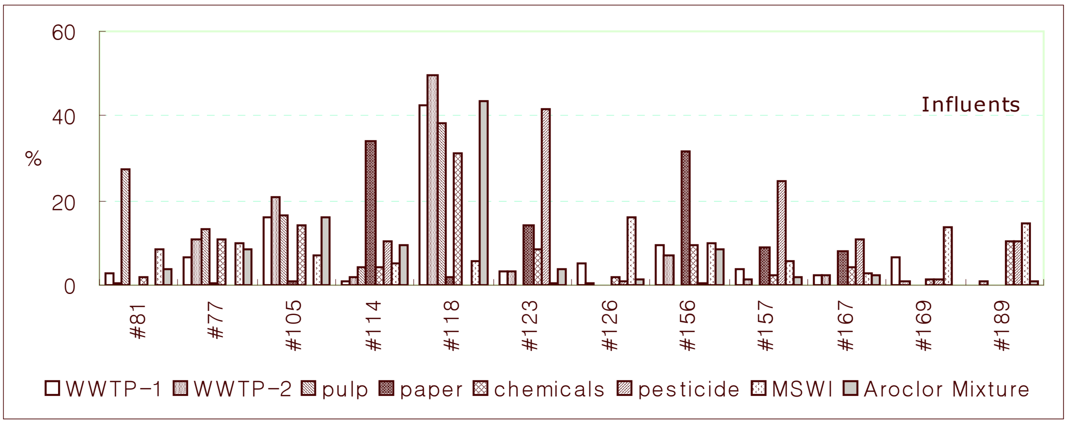
- 1) WWTP-1: Domestic wastewater treatment plant. 2) WWTP-2: Domestic and industrial wastewater treatment plant. 3) MSWI: Scrubbing water was collected. 4) d.w.: dry weight. 5) RE (%)= [($C_{IN}$-$C_{OUT}$)]*100/$C_{IN}$, where $C_{IN}$ and $C_{OUT}$ are concentrations of coplanar PCBs in influent and effluent, respectively.

than 6, the results of this study were almost consistent with Byrns' study except for industrial wastewater from pulp manufacturing facility. As shown in Table 1, since the removal efficiency of coplanar PCBs was as high as 89.1% in pulp manufacturing, even though coplanar PCBs in SS accounted for only 18.1 % of influent concentration, others could be thought as removal mechanisms in addition to adsorption.

Figure 1 shows the congener patterns of coplanar PCBs in raw wastewaters of discharge facilities studied. Each congener pattern of discharge facilities has different characteristics, and then which suggests different formation mechanisms and contamination sources of PCBs in each discharge facility. The dominant congeners out of 12 coplanar PCBs in raw wastewater were 3,4,4',5-TetraCB (#81) and 2,3',4,4',5-PentaCB (#118) in pulp, 2,3,4,4',5-PentaCB (#114) and 2,3,3',4,4',5-HexaCB (#156) in paper, and 2',3,4,4',5-PentaCB (#123) and 2,3,3',4,4',5'-HexaCB (#157) in pesticide manufacture, respectively.

Scrubbing water of MSWI contained 3,3',4,4',5-PentaCB (#126) and 3,3',4,4',5,5'-HexaCB (#169), which were contained in ambient air and flue gas from thermal plants such as incinerator[8,9], but these congeners were not contained in commercially-produced Aroclor. As shown in Figure 1, contribution percentiles of these congeners (#126 and #169) in most of raw wastewaters were less than 5 % of total coplanar PCBs except for that in scrubbing water.

The congener patterns of coplanar PCBs in raw wastewater of domestic WWTP-1 were similar to that of Aroclor mixtures (1242/1248/1254/1260), and the dominant congeners were 2,3',4,4',5-PentaCB (#118) and 2,3,3',4,4'-PentaCB (#105) like Aroclor. But, the raw wastewater of domestic WWTP-1 also contained two congeners of 3,3',4,4',5-PentaCB (#126) and 3,3',4,4',5,5'-HexaCB (#169). This result was coincident with the previous



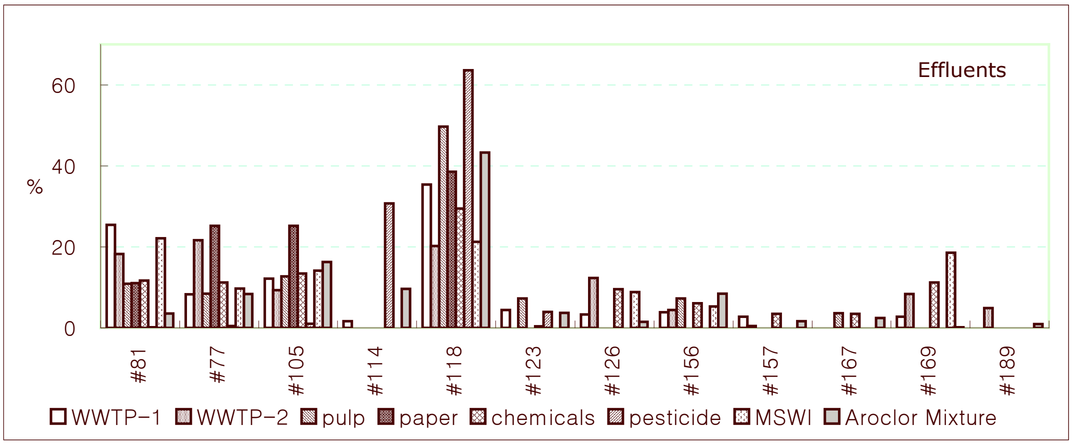




Figure 1. Congener patterns of coplanar PCBs in influents and effluents of wastewater treatment plants.

study[10] that major sources of PCBs load into domestic wastewater are basically the use of commercial PCBs in the past and atmospheric deposition.

Meanwhile, it will be useful to know the congener patterns of coplanar PCBs, i.e. the fingerprints of influent and effluent such as Figure 1 in order to identify the discharge sources of wastewater flowing into surface water. Despite of the high removal efficiencies of coplanar PCBs in WWTPs, since a portion of coplanar PCBs enters the aquatic environment and soil, in this study we reviewed the discharge characteristics of coplanar PCBs from a few wastewater discharge facilities. But it is further needed to study mass balance in order to estimate the total input of coplanar PCBs into aquatic environment and soil from effluents and sludges.

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