DISTRIBUTION PATTERNS OF DIOXIN LIKE PCBS (DL-PCBS) IN SURFACE SEDIMENTS FROM THE FOUR MAIN RIVER BASINS IN KOREA

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Abstract

This paper was performed to investigate the concentration levels and to identify the possible sources of 12 dioxin like polychlorinated biphenyls (DL-PCBs, IUPAC number PCB-77, 81, 105, 114, 118, 123, 126, 156, 157, 157, 167, 169 and 189) in sediment from four main river basins (i.e., rivers and lakes) in Korea including Han river, Nakdong river, Geum river and Yeongsan river. In Korea, riverine and lacustrine waters have been mainly used as the source of water supply not only industrial and agricultural usage but also tap water for public. Therefore, it is important to analyze the residual hazardous micro-pollutants in water environment. In this study, the overall concentration of DL-PCBs of 83 lake sediment samples were in the range of 4.292 - 461.1 pg/g-dry (0.000 - 0.568 pg TEQ/g-dry) and in case of 135 river sediment samples, the concentration ranged from 1.809 to 124292.4 pg/g-dry (0.000 - 41.19 pg TEQ/g-dry). Penta-CBs (#118 and #105), major components among 12 DL-PCBs contained in commercial PCB products, were the most dominant (over 65%) congeners in sediment.

Introduction

Twelve dioxin like PCBs (DL-PCBs) are well known for their carcinogenic potential and bioaccumulation in biota and human body through dietary intake, inhalation and other indirect exposure as other persistent organic pollutants[1]. The contamination of DL-PCBs has been detected in various environmental matrices including water, air and soil. Especially, the contamination of sediment is highly concerned because it is a primary source of retaining organic pollutants to benthic microorganisms. There have been several reports about the level of DL-PCBs in Korean river or coastal sediments of specific region but no remarkable trial was performed to identify source of their occurrences in nation-wide scale at a same time. Therefore, this paper pursued to profile the sources of DL-PCBs of four main river basins based on statistical analysis with comparing distribution patterns of DL-PCBs between the sediment samples and ambient air, flue gas and commercial products.

Materials and Methods

Sampling and sample preparation

Sampling was performed at Han river, Nakdong river, Geum river and Yeongsan river basins in 2008. Basically, the sampling sites for surface sediment samples were decided based on Korean basic monitoring network (111 sites in river and 28 sites in lake). Stainless steel Petite Ponar® grab sampler was used and undisturbed part of 2cm deep surface sediments was transferred into 1 L amber glass bottle in icebox. All samples were air-dried at room temperature and sieved using a 230 mesh sieve after grinded using mortar and pestle. All prepared samples were stored in refrigerator until analyzed[2].

Analytical procedure

DL-PCBs in sediment were analyzed with the analytical method of endocrine disrupting chemicals developed by NIER (2002) and EPA method 1668 (US EPA, 2001) with minor modifications. Briefly, sediment samples (~10 g) were extracted with accelerated solvent extractor (ASE-200; CA, USA) using acetone:hexane (v/v, 1:1) and $^{13}C_{12}$-labelled DL-PCBs were spiked into the extract as internal standards. Then, the extract was cleaned up with multilayer silica gel column. The amount of DL-PCBs was measured by HRGC/HRMS (Agilent 6890 GC/JMS 800D, Japan) with a 60 m DB-5MS capillary column (J&W Scientific, USA). Recoveries of $^{13}C_{12}$-labelled DL-PCBs were within 60-94%. The limit of quantification (LOQ) set on a signal-to-noise ratio of 10 was 0.1 pg/g-dry. All multivariate statistical analyses including principal component analysis (PCA) and hierarchical cluster analysis (HCA) were performed by SPSS 14.0K (SPSS inc., USA).

Results and Discussion:

The concentration levels and distribution patterns of DL-PCBs in sediment

DL-PCBs are detected in all of sediment samples. Overall detected concentration of DL-PCBs of lakes was in the range of 4.29 - 461.1 pg/g-dry (mean: 58.3 pg/g-dry) and 0.00 - 0.57 pg TEQ/g-dry (mean: 0.04 pg/g-dry). The highest concentration was detected in the lake sediment samples located in the vicinity of waste water treatment plants and metropolitan city that both were known as emission sources of DL-PCBs[3]. There is no sediment quality guideline on DL-PCBs in Korea; so the result was compared with ERL (Effects Range-Low; 22700 pg/g-dry) and ERM (Effects Range-Median; 180000 pg/g-dry) developed by National Oceanic and Atmospheric Administration[4.] The DL-PCBs levels in this study were below the values of ERL and ERM. In case of sediment samples taken at rivers, the concentration ranges were wide as 1.809 - 124292.4 pg/g-dry (mean: 1135.680 pg/g-dry) and 0.000 - 41.189 pg TEQ/g-dry (mean: 0.426 pg/g-dry)**.** The highest concentration was above ERL and even reached 70% of ERM value. However, only three samples had shown abnormally higher levels than the each river basin average, so the concentrations of DL-PCBs in most sampling sites were below the ERL. Relative geographic information or possible originating sources were not found in these three notably high concentration sample sites so further monitoring seems to be needed. The levels of DL-PCBs at this study are similar or relatively lower than other countries with the assumption that 5% of total PCBs amounts will contribute on DL-PCBs values. The global levels of PCBs in sediments are reported that 20.8 - 1760 ng/g-dry of Narragansett Bay in USA, 0.9 - 1210 ng/g-dry of Alexandria harbor in Egypt, 10 - 899 ng/g-dry of Naples harbor in Southern Italy and 0.62 - 337 ng/g-dry of Songhua River in Northeast China[5]. Therefore, we can tell that the contamination of DL-PCBs in sediments of four river basins of Korea is not so critical until now. The observed distribution pattern was similar between river and lake sediment samples. The most dominant congener detected at lake sediment was Penta-CB (#118) as 49.97±8.24% followed by Penta-CB (#105) of 20.7±3.92%, Tetra-CB (#77) of 12.6±8.72% and Hexa-CB (#156) of 8.78±4.25%. In case of river sediment, PCB-118 was most dominant (57.6±14.65%) and PCB-105 (23.99±8.61%), PCB-77 (14.42±10.54%) and PCB-156 (8.09±2.51%) in order. According to Takasuga et al. (2006)[6], these two predominant Penta-CBs were commonly used for PCB commercial products like most Kanechlor and/or Aroclor except Aroclor-1260, -1262, Kanechlor-600 and Clophen-60. In addition, Sakai et al. (2001)[7] reported that PCB congeners 105, 114 and 118 are dominated in bulk deposition samples from ambient air. Therefore, it can be conjectured that that the usage of PCBs commercial products and air deposition plays a role in sediment as a PCB source.

The sources of DL-PCBs in sediment

To investigate the correlations between sediment samples and PCB containing substances as PCBs sources, we selected 72 samples among total 210 river and lake samples based on the detection frequency of 12 congeners (i.e., over 7 congeners). To identify possible sources of PCBs, principal component analysis (PCA) and hierarchical cluster analysis (HCA) were performed with the proportion of each PCBs congener in samples and that of commercial products (6 Aroclor mixtures, USA; 6 Kanechlor mixtures, Japan; 4 Clophen mixtures, Germany; 1 Sovol mixture, Russia), incinerator flue gas and ambient air[8]. As seen in Fig. 1, two principal components (PCs) were created. PC 1 showed negative relations with Tetra-CB (#81 and #77), Penta-CB (#126) and Hexa-CB (#169) known as originating from general combustion process and Penta-CBs (#114, #105 and #118) known as depositing from ambient air to sediments. PC 2 showed negative relations with pretty dominant congeners like Penta-CBs (#105 and #118) whereas showing positive relations with scarcely detected congeners like Tetra-CB (#81), Penta-CBs (#114 and #126) and Hexa-CB (#169). Therefore, we can separate the 72 samples with difference of originating source by PC 1 and with difference of congener distribution pattern by PC 2. Consequently, four groups were created as following; 59 samples and 7 commercial products including Sovol, Clophen-50, Aroclor-1254 and 4 Kanechlor mixtures as Group 1, 12 samples and 7 commercial products including 3 Aroclor, 2 Kanechlor and 2 Clophen mixtures as Group 2, only one lake sample of Han river basin with Arochlor-1260, -1262 and Chlophen-60 as Group 3 and at last ambient air and flue gas as Group 4. Any sediment samples were not clustered with Group 4 so PCBs in sediment were thought to be originated mainly from commercial products. When comparing PCBs distribution patterns of each group, Group 1 and 2 had similarities and located at the vicinity of the scatter diagram in Fig. 1 but Group 3 and 4 showed apparent different patterns with two former groups. Specifically, the samples of Group 1 showed similar pattern with Kanechlor-MIX and Kanechlor-500. Group 2 samples had similar patterns with Kanechlor-300 and Group 3 with Clophen-60. So, we could infer that Kanechlor mixtures have the largest impacts on Korean river basin. At hierarchical analysis to see the closeness among samples and comparing substances, Kanechlor mixtures, mainly used for transformer oil in Korea[8] showed closer relationship than Sovol and Clophen mixtures also. Therefore, the strongest influencing source seemed to be commercial PCBs products. Though, there still remained possibility of air degradation effects to DL-PCBs sedimentation. Penta-CB (#126) is not involved in any commercial PCB products only except for Aroclor-1242[9] and it was found at forty among 72 samples. Also, Hexa-CB (#169) well known as originated from combustion process also was detected in 5 samples each from Group 1 and 2. This indicates that even the Group 1 and 2 didn't gather with air or flue gas directly but still has some relationship with air deposition as PCB source. However, when comparing a distribution pattern of Group 1 and 2 with the pattern of Group 4, we can see the reverse pattern change. The heavier congeners like Hexa- or Hepta-CBs of Group 1 and 2 were tend to be decreased than Group 4 but lighter congeners like Tetra-CBs of Group 1 and 2 were tend to be increased than Group 4, simultaneously. This reverse distribution pattern change of relative heavier congeners comparing with lighter congeners might be happened because of degradation process of higher chlorinated PCB congeners in sediments[10]. Therefore, it is likely that there are also impacts by degradation and deposition from air or flue gas not only from impacts by commercial PCB products.

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Table 1. Concentration levels of dioxin like PCBs in surface sediments

Compound \ Sampling site		River basin[a] (unit : pg/g-dry , pg WHO-TEQ/g-dry[b])							
		HR	HL	NR	NL	GR	GL	YSR	YSL
12 total DL- PCBs (WHO-TEQ)	min	1.809 (0.000)	6.355 (0.000)	4.185 (0.000)	4.292 (0.000)	3.171 (0.000)	7.345 (0.000)	5.132 (0.000)	5.733 (0.000)
	max	6778.7 (0.232)	249.33 (0.332)	7716.5 (10.082)	461.10 (0.568)	130.19 (0.124)	133.33 (0.136)	124292 (41.189)	123.36 (0.012)
	mean	234.18 (0.019)	67.085 (0.046)	281.53 (0.303)	52.193 (0.060)	23.699 (0.010)	54.604 (0.022)	4803.2 (1.600)	33.738 (0.003)
	S.D.	1157.0 (0.050)	59.109 (0.073)	1262.7 (1.640)	91.713 (0.128)	27.464 (0.029)	38.267 (0.043)	24371 (8.075)	37.061 (0.004)
	DF[c]	34/34	34/34	38/38	22/22	29/29	15/15	27/27	11/11

[a]HR/L, river/lake sample of Han river basin; NR/L, river/lake sample of Nakdong river basin; GR/L, river/lake sample of Geum river basin; YSR/L, river/lake sample of Yeongsan river basin; [b]Based on the WHO (World health organization) 2005 TEF (Toxic equivalent factor), [c]DF = Detection frequency of dioxin-like PCBs at each river and lake sample group

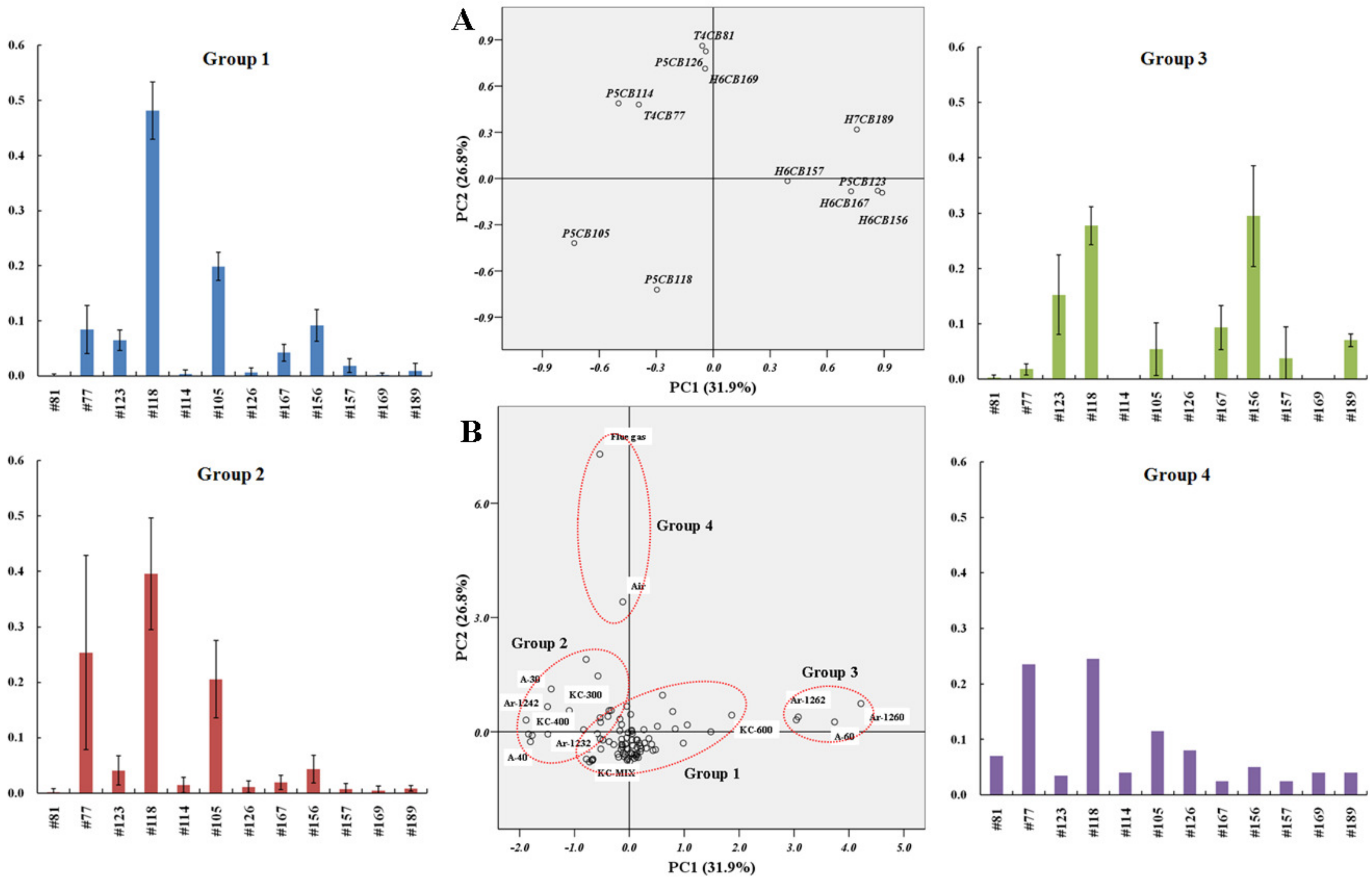

Fig. 1: Scatter diagram (A) and loading plot (B) and distribution patterns of DL-PCBs in sediment