Concentration and distribution of polychlorinated biphenyls in rice paddy soils

Leesun Kim 1 · Jin-Woo Jeon 2 · Ji-Young Son 2 · Min-Kyu Park 2 · Chul-Su Kim 3 · Hwang-Ju Jeon 1 · Tae-Hoon Nam 1 · Kyeongnam Kim 1 · Byung-Jun Park 4 · Sung-Deuk Choi 2,3 · Sung-Eun Lee 1

Received: 5 January 2017 / Accepted: 3 February 2017 / Published online: 14 March 2017
© The Korean Society for Applied Biological Chemistry 2017

Abstract To monitor and evaluate the risk of polychlorinated biphenyls (PCBs) contamination in Pohang, Korea, the concentration and distribution of 29 PCBs in paddy soils were determined using high-resolution gas chromatography/high-resolution mass spectrometry. The overall concentrations of \( \Sigma_{29} \) PCBs in the paddy soils of the areas close to the heavily industrial city of Pohang (268–1833 pg g\(^{-1}\) dw) were higher than those in the paddies from Anseong (106.6–222.6 pg g\(^{-1}\) dw) in Korea. In Pohang, the major contributors to the \( \Sigma_{29} \) PCBs were the non-dioxin-like PCBs, including the PCBs 28, 52, 70, 101, 118, 138, 153, and 180, which correspond to 48–62% of the total PCBs. The toxic equivalency (TEQ) values obtained from the 12 dioxin-like PCBs from Pohang (0.03–1.03 pg TEQ g\(^{-1}\) dw) showed that PCB 126 contributed the highest toxicity, possibly posing a risk to the living organisms. The results of both principal component and cluster analysis based on the PCB homologue patterns demonstrated that each sampling site showed a similar PCBs contamination pattern, and Aroclor 1254, which is likely used by small and big steel factories, was identified as a major source of PCB contamination in Pohang.

Keywords Industrial area · Monitoring · Pohang · Polychlorinated biphenyls

Introduction

Since the late 1920s, the synthesized polychlorinated Biphenyls (PCBs) have been used in many industries, including petrochemical refineries, shipbuilding, and steel. The PCBs were defined as persistent organic pollutants (POPs) [1] because they do not easily degrade in the environment, causing adverse effect on the living organisms including humans. The PCB congeners are generally classified into two groups: dioxin-like (DL)-PCBs and non-dioxin-like (NDL)-PCBs. The toxicities of DL-PCBs have been exhaustively investigated, and the toxicity equivalency factors (TEF) values were assigned to DL-PCBs for health risk assessment [2] because they do not easily degrade in the environment, causing adverse effect on the living organisms including humans. The PCB congeners are generally classified into two groups: dioxin-like (DL)-PCBs and non-dioxin-like (NDL)-PCBs. The toxicities of DL-PCBs have been exhaustively investigated, and the toxicity equivalency factors (TEF) values were assigned to DL-PCBs for health risk assessment. In contrast, the toxicological characterization of NDL-PCBs is still needed for the complete health risk assessment [2] because their high percentages are also found in food and human samples [3–5]. The NDL-PCBs 138, 153, and 180 are relatively less hydrophobic, because of which they are less strongly bound to the sediments, and are more easily available to the aquatic living organisms. According to a previous study, the exposure to the NDL-PCBs 101, 153, and 180 propelled the escalation of oxidative stress in chondrocytes by reducing their antioxidant ability [6].
It was estimated that the amount of \( \Sigma_{22} \) PCBs released worldwide from 1930 to 2016 was 0.1 Mt [7]. Even though PCBs have never been produced in Korea, 0.3 tons of \( \Sigma_{22} \) PCBs was emitted into the atmosphere from 1946 to 2015 primarily because of the importation of the PCB-containing equipment to Korea for several industrial usages [7]. The previous studies on the sources of PCB contamination reported that the municipal solid waste incinerators and iron and steel industries were the major emitters of dioxins, such as PCBs, in Korea as well as other countries. A previous study demonstrated that the high levels of PCBs were derived from the steel complex [8]. Furthermore, a study on the soil samples from the rural, city, and industrial sites in Ulsan, Korea, suggested that the high levels of PCBs might be strongly related to the surrounding industrial complexes, including the shipbuilding industry and petrochemical refinery [9]. However, to the best of our knowledge, only a few studies have been carried out to determine the concentrations of PCBs in the paddy soils of Korea, even though rice is the main staple food of Korea. Given that the soil is an essential reservoir of atmospherically deposited PCBs, which might be transported into the food web, the determination of the PCB levels and distributions in paddy soils is urgently required to protect human health and living organisms in the heavily industrial areas. According to a recent study on PCBs in the paddy soils nearby a transformer oil-related factory in Anseong, Korea, the \( \Sigma_{29} \) PCBs concentrations ranged from 106.65 to 222.67 pg g^{-1} dw [10], which were not the high-risk values.

The PCB levels in the soils nearby industrial areas were investigated by many researchers around the world, because the vegetables or grains grown in an area are deeply linked to the public health [11, 12]. It was reported that the \( \Sigma_{33} \) PCB concentrations in wheat, rice, soil, and air from Pakistan were 0.15–2.22, 0.05–9.21, 0.70–30.5 ng g^{-1} dw, and 41–299 pg m^{-1}, respectively [11].

The objectives of this research were (1) to perform the monitoring of PCBs in the rice paddy soils from Pohang, one of the highly polluted industrial cities in Korea, by determining the concentration of 29 PCB congeners and homologue patterns, (2) to perform the risk assessment using the TEF system, and (3) to uncover the PCB contamination sources using the principal component analysis (PCA) and clustering analysis (CA).

Materials and methods

Sample preparation and instrumental analysis

Rice paddy soils (0–10 cm) were sampled from 20 sites in Pohang City, Gyeongsang Province, Korea. The sampling locations in Pohang are shown in Fig. S1, and the grid references are listed in Table S1. The world’s fourth largest steel producer, POSCO, was established in Pohang with a population of 0.52 million in 1968. Now, Pohang is one of the biggest industrial cities with many small and big steel makers in Korea.

Before being passed through a 2-mm sieve, the soil samples were air-dried at the room temperature. The Soxhlet extraction was performed on the 10-g soil samples with the optimized sample preparation procedure and gas chromatography/high-resolution mass spectrometry described in our previous study. The United States Environmental Protection Agency (US EPA) criteria (method 1668C) were used to analyze each PCB congener. The quantification of the chemicals was carried out by using the isotope dilution method with calibration standards (EC9605-CVS and 68C-CVS, Wellington Laboratories, Canada). The compounds of interest were 12 DL-PCBs (77, 81, 126, 169, 105, 114, 118, 123, 156, 157, 167, and 189), 6 indicator PCBs (28, 52, 101, 138, 153, and 180), and 14 NDL-PCBs (33, 44, 52, 70, 81, 114, 118, 128, 170, 187, 194, 195, 199, and 206). The recovery rates of the surrogate standards ranged from 62.2 to 110.8%.

Calculation for toxic equivalency quantities (TEQ)

The TEF system was used for the risk assessment of PCB congeners found in this study. The overall toxicity, or the toxic equivalency (TEQ), of a mixture was calculated by adding the concentrations of all congeners (\( C_i \)) and multiplying by its TEF(\( \frac{1}{C_{138}} \) / \( C_{2} \) [13].

\[
\text{TEQ} = \Sigma[C_i] \times \text{TEF}_i
\]

Statistical analysis

Two hypotheses were developed for this study. First, each sampling site from Pohang has the same tendency of PCB contamination. Second, the PCB contaminations were derived from the Aroclors 1254 and 1260 used in the industrial activities in Pohang. These two hypotheses were verified based on the results derived from both PCA and CA with a statistical package for the social sciences (IBM SPSS 23, USA). The score and loading values obtained from the PCA analysis were used for visualization with the score and loading plots. The profiles of each PCB homologue group (tri-, tetra-, penta-, hexa-, hepta-, octa-, and nonaCBs) obtained from this study and those of the Aroclors 1242, 1254, and 1260 from a previous study [14] were used for the statistical analyses. The different rates of the Aroclor profiles produced by different companies were utilized for the statistical analyses. The concentration of...
each homologue was normalized by the concentration of $\Sigma_{29}$ PCBs for each sample. The identification of the PCB sources in Pohang was based on the data from PCA and CA. To assess the differences between the PCB concentrations of the sites and cities, the rank-sum tests were performed using SigmaPlot 12.5 (Systat Software, USA). Differences were considered to be statistically significant if the “$p$ value” was less than 0.05.

Results

$\Sigma_{29}$ PCBs, 7 PCBs, and toxic equivalency quantities of 12 DL-PCBs

The concentrations of $\Sigma_{29}$ PCBs (Table S2) at 20 sites in Pohang ranged from 268 to 1833 pg g$^{-1}$ dw. Site 10 (1838 pg g$^{-1}$ dw) and site 17 (1834 pg g$^{-1}$ dw) showed the highest PCB concentrations, and site 14 (1281 pg g$^{-1}$ dw) and site 12 (1248 pg g$^{-1}$ dw) showed the second highest PCB concentrations. Out of the 29 PCB congeners determined, the PCBs 28, 52, 70, 101, 118, 138, 153, and 180 were dominating (mean: 39–80 pg g$^{-1}$ dw) in the most sampling sites. These congeners, except for PCB 70, were known to be the indicator PCBs. The indicator PCBs detected in this study accounted for 48–63% of the $\Sigma_{29}$ PCBs, except for site 8 (34%).

The TEQ values for the 12 DL-PCBs at each site from Pohang were calculated based on the TEQ calculation formulae. The TEQ values (Table 1) ranged from 0.03 to 1.03 pg TEQ g$^{-1}$ dw. Site 7 showed the highest TEQ value (1.03 pg TEQ g$^{-1}$ dw) and site 12 the second highest (0.89 pg TEQ g$^{-1}$ dw).

Distribution and possible source identification of PCBs

Among the homologues determined for each sampling site from Pohang (Fig. 1), the pentaCBs (mean 21.0%) and hexaCBs (mean 25.3%) were the most dominant, followed by the tetraCBs (mean 18.3%) and triCBs (mean 18.0%). Based on these PCB homologue profiles, the PCB contamination in Pohang was found to be more associated with Aroclor 1254 than with Aroclors 1260 and 1242. This was supported by the results of PCA (Fig. 2).

Discussion

Recently, many unexpected compounds in the environments have been determined using advanced instruments [15, 16], and in this study, all PCBs were determined using high-resolution mass spectrometry (HR-MS) in conjunction with gas chromatography.

### Table 1

| PCBs | PCBs concentration (pg g$^{-1}$) for each sampling site |
|------|-------------------------------------------------------|
| 1    | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
| Non-ortho-substituted PCBs | | | | | | | | | | | | | | | | | | | | |
| 77  | 0.0003 | 0.0004 | 0.0005 | 0.0006 | 0.0007 | 0.0008 | 0.0009 | 0.0010 | 0.0011 | 0.0012 | 0.0013 | 0.0014 | 0.0015 | 0.0016 | 0.0017 | 0.0018 | 0.0019 | 0.0020 | 0.0021 |
| 81  | 0.0007 | 0.0008 | 0.0009 | 0.0010 | 0.0011 | 0.0012 | 0.0013 | 0.0014 | 0.0015 | 0.0016 | 0.0017 | 0.0018 | 0.0019 | 0.0020 | 0.0021 | 0.0022 | 0.0023 | 0.0024 | 0.0025 | 0.0026 |
| 126 | 0.0022 | 0.0023 | 0.0024 | 0.0025 | 0.0026 | 0.0027 | 0.0028 | 0.0029 | 0.0030 | 0.0031 | 0.0032 | 0.0033 | 0.0034 | 0.0035 | 0.0036 | 0.0037 | 0.0038 | 0.0039 | 0.0040 | 0.0041 |
| 169 | 0.0028 | 0.0029 | 0.0030 | 0.0031 | 0.0032 | 0.0033 | 0.0034 | 0.0035 | 0.0036 | 0.0037 | 0.0038 | 0.0039 | 0.0040 | 0.0041 | 0.0042 | 0.0043 | 0.0044 | 0.0045 | 0.0046 | 0.0047 |
| Mono-ortho-substituted PCBs | | | | | | | | | | | | | | | | | | | | |
| 105 | 0.0001 | 0.0002 | 0.0003 | 0.0004 | 0.0005 | 0.0006 | 0.0007 | 0.0008 | 0.0009 | 0.0010 | 0.0011 | 0.0012 | 0.0013 | 0.0014 | 0.0015 | 0.0016 | 0.0017 | 0.0018 | 0.0019 | 0.0020 |
| 123 | 0.0002 | 0.0003 | 0.0004 | 0.0005 | 0.0006 | 0.0007 | 0.0008 | 0.0009 | 0.0010 | 0.0011 | 0.0012 | 0.0013 | 0.0014 | 0.0015 | 0.0016 | 0.0017 | 0.0018 | 0.0019 | 0.0020 | 0.0021 |
| 157 | 0.0003 | 0.0004 | 0.0005 | 0.0006 | 0.0007 | 0.0008 | 0.0009 | 0.0010 | 0.0011 | 0.0012 | 0.0013 | 0.0014 | 0.0015 | 0.0016 | 0.0017 | 0.0018 | 0.0019 | 0.0020 | 0.0021 | 0.0022 |
| 181 | 0.0004 | 0.0005 | 0.0006 | 0.0007 | 0.0008 | 0.0009 | 0.0010 | 0.0011 | 0.0012 | 0.0013 | 0.0014 | 0.0015 | 0.0016 | 0.0017 | 0.0018 | 0.0019 | 0.0020 | 0.0021 | 0.0022 | 0.0023 |
| $\Sigma$ | | | | | | | | | | | | | | | | | | | | |
Of the 20 sampling sites, the mean $\Sigma_{29}$ PCB concentration of sites 11–20 (group 2) (940 pg g$^{-1}$ dw) was higher than that of the remaining sites (group 1) (550 pg g$^{-1}$ dw); this was supported by the statistical analysis (Mann–Whitney rank-sum test, $p < 0.05$) (Fig. S1). It is believed that this finding was strongly linked with the location of each site because the sites in group 2 were located near the steel industry complex, compared with those in group 1.

The residual concentrations of the $\Sigma_{29}$ PCBs in the soil samples from Pohang (268–1833 pg g$^{-1}$ dw) were much higher than those (107–223 pg g$^{-1}$ dw) from Anseong [10]. The $\Sigma_{29}$ PCB concentrations from Pohang were lower than the high-risk PCB levels for residential (0.23 mg kg$^{-1}$) and industrial (0.94 mg kg$^{-1}$) soil setup by US EPA [17].
The major contributors to the $\Sigma_{29}$ PCBs in Pohang were NDL-PCBs, including PCB 28, 52, 70, 101, 118, 138, 153, and 180, which corresponded to 48–62% of the total. Combined contribution of PCB 153 and 138 to the sum of the 7 indicators was more than 30%, which was consistent with the previous studies showing the high percentages of the congeners in food groups such as fish [18, 2]. Brazova et al. demonstrated that the PCBs 153 and 138 were the biggest contributors to the sum of 6 indicators in European catfish. Another study also showed that PCB 153 contributed 53% to the sum of NDL-PCBs in catfish [4], because the PCB mixture released by various industrial activities surrounding the lake reflected fish contamination. In this study, the congener patterns of soil contamination should also reflect the presence of the congeners in the atmosphere, closely associated with unintentional emissions due to the historical use of commercial PCB mixtures by the steel industry. The presence of abundant congeners was also derived from their persistent properties (approximately 10-year half-life for PCB 101, 7 years for PCB 118, and 18 years for both PCBs 138 and 153) [19].

The DL-PCB congener distribution in the soil samples showed the predominance of PCBs 118, 105, 156 and 77 (49, 23, 9, and 9%, respectively) in terms of concentration, which was in agreement with the previous studies on PCBs in fish [4]. Even though the concentration of PCB 126 was low, the congener contributed highly to the TEQ values at all soil sampling sites from Pohang (90%). The DL-PCB TEQ values in Pohang (0.03–1.03 pg TEQ g$^{-1}$ dw) were higher than those in Anseong (0.04–0.11 ng TEQ kg$^{-1}$ - dw), but much lower than those of the agricultural soils in Delhi, India (0.01–105.54 pg g$^{-1}$) [20], as well as the WHO threshold level (20 ng TEQ kg$^{-1}$).

The measured values of 0.03–1.03 pg TEQ g$^{-1}$ are much lower than the physiological effects of PCBs in livers of aquatic mammals as 160–1400 pg TEQ g$^{-1}$ [21]. Kannan et al. [21] measured the toxicity level of the PCBs in seals, European otters, and mink. However, they suggested that the dietary threshold levels could be 1.4–1.9 pg TEQs g$^{-1}$. On the other hand, [22] also showed that the TEQ level as 10 ng TEQ (BaP) g$^{-1}$ caused DNA damage in earthworms (Eisenia fetida). With this regard, the TEQ levels determined in Pohang seem to be safe to animals including humans because of lower levels than the previous studies.

**Distribution and possible source identification of PCBs**

The pentaCBs and hexaCBs were detected as the two most dominant homologues in the soil samples from Pohang, which was consistent with the results from Anseong [10]. The triCBs and tetraCBs also presented high ratios, indicating the possible degradation of the highly chlorinated PCBs. However, the PCB homologue pattern was more associated with Aroclor 1254 than with Aroclors 1260 and 1242, which was confirmed by the data obtained from PCA (Fig. 2) and CA (Fig. S2). For source identification, the proportions of each homologue group identified in the soil samples from Pohang and commercial products (Aroclors 1242, 1254, and 1260) [14] were compared. The technical mixtures used for the statistical tests were known to be the transformer oils mostly consumed in the Korean power stations [23]. According to the result of PCA (Fig. 2) obtained from the PCB profiles, the variances of the first and second principal components were 57 and 28%, respectively. The score plot demonstrated the first hypothesis that all soil samples were closely related to each other and with Aroclor 1254 (1 and 2), which was confirmed by CA. The dendrogram indicated that Pohang and Aroclor 1254 (1 and 2) were classified into group 1. The Aroclors 1260 (1, 2, and 3) and 1242 (1, 2, and 3) were classified into groups 2 and 3, respectively, because the PCB profiles of each Aroclor with the same number were slightly different [24]. The PCA loading plot also confirmed that the soil samples and Aroclor 1254 were characterized with tetra-, penta-, and hexaCBs. These plots showed that the octaCBs contributed highly to Aroclor 1260, and the triCBs and tetraCBs were big contributors to Aroclor 1242.

**Acknowledgments** This research was carried out under the Cooperative Research Program for Agricultural Science and Technology Development (Project No. PJ010922032015), Rural Development Administration, Republic of Korea.

**Compliance with ethical standards**

**Conflict of interest** The authors have declared that no competing interests exist.

**References**

1. Stockholm Convention (2008) The 12 initial POPs under the Stockholm Convention http://chm.pops.int/TheConvention/ThePOPs/The12InitialPOPs/tabid/296/Default.aspx. Accessed 14 Apr 2016
2. EFSA (2010) Scientific report of EFSA—results of the monitoring of dioxin levels in food and feed. EFSA J 8:1385
3. Liang B, Liu X, Hou J, Liang G, Gong W, Xu D, Zhang L (2014) PCBs levels and indicator congeners in children’s and adolescents’ hair. Environ Pollut 185:10–15
4. Squadrone S, Prearo M, Nespoli R, Scanzio T, Abete MC (2016) PCDD/Fs, DL-PCBs and NDL-PCBs in European catfish from a northern Italian lake: the contribution of an alien species to human exposure. Ecotox Environ Safe 125:170–175
5. Wingfors H, Lindström G, van Bavel B, Schuhmacher M, Hardell L (2000) Multivariate data evaluation of PCB and dioxin profiles in the general population in Sweden and Spain. Chemosphere 40:1083–1088
6. Abella V, Santoro A, Scotece M, Conde J, López-López V, Lazzaro V, Gómez-Reino JJ, Meli R, Gualillo O (2015) Non-dioxin-like polychlorinated biphenyls (PCB 101, PCB 153 and PCB 180) induce chondrocyte cell death through multiple pathways. Toxicol Lett 234:13–19
7. Breivik K, Sweetman A, Pacyna JM, Jones KC (2007) Towards a global historical emission inventory for selected PCB congeners—a mass balance approach: 3. An update. Sci Total Environ 377:296–307
8. Baek SY, Choi SD, Park H, Kang JH, Chang YS (2010) Spatial and seasonal distribution of polychlorinated biphenyls (PCBs) in the vicinity of an iron and steel making plant. Environ Sci Technol 44:3035–3040
9. Nguyen TNT, Kwon H-O, Lee Y-S, Kim L, Lee S-E, Choi S-D (2016) Spatial distribution and source identification of indicator polychlorinated biphenyls in soil collected from the coastal multi-industrial city of Ulsan, South Korea for three consecutive years. Chemosphere 163:184–191
10. Kim L, Jeon J-W, Lee Y-S, Jeon H-J, Park B-J, Lee H-S, Choi S-D, Lee S-E (2016) Monitoring and risk assessment of polychlorinated biphenyls (PCBs) in agricultural soil collected in the vicinity of an industrialized area. Appl Biol Chem 59:655–659
11. Mahmood A, Syed JH, Malik RN, Zheng Q, Cheng Z, Li J, Zhang G (2014) Polychlorinated biphenyls (PCBs) in air, soil, and cereal crops along the two tributaries of River Chenab, Pakistan: concentrations, distribution, and screening level risk assessment. Sci Total Environ 481:596–604
12. Zhu Z-C, Chen S-J, Zheng J, Tian M, Feng A-H, Luo X-J, Mai B-X (2014) Occurrence of brominated flame retardants (BFRs), organochlorine pesticides (OCPs), and polychlorinated biphenyls (PCBs) in agricultural soils in a BFR-manufacturing region of North China. Sci Total Environ 481:47–54
13. Safe SH (1998) Hazard and risk assessment of chemical mixtures using the toxic equivalency factor approach. Environ Health Persp 106:1051–1058
14. Frame GM, Cochran JW, Bowadt SS (1996) Complete PCB congener distributions for 17 arocal mixtures determined by 3 HRGC systems optimized for comprehensive, quantitative, congener-specific analysis. J High Resol Chromatogr 19:657–668
15. Kim J-Y, Choi J-Y, Yoon C-Y, Cho S, Kim WS, Do JA (2015) LC–MS/MS monitoring of 22 illegal antihistamine compounds in health food products from the Korean market. J Korean Soc Appl Biol Chem 58:137–147
16. Ko A-Y, Abd El-Aty AM, Jang J, Choi J-H, Rahman MM, Kim S-W, Shin H-C, Shim J-H (2015) Detecting fludioxonil residues in brown rice and rice straw using gas chromatography-nitrogen phosphorus detector. J Korean Soc Appl Biol Chem 58:213–217
17. EPA (2016) Regional Screening Levels (RSLs)—Generic Tables (May 2016). US Environmental Protection Agency. https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables-may-2016. Accessed 20 Oct 2016
18. Brazova T, Hanelova V, Miklisova D (2012) Bioaccumulation of six PCB indicator congeners in a heavily polluted water reservoir in Eastern Slovakia: tissue-specific distribution in fish and their parasites. Parasitol Res 111:779–786
19. Sinkkonen S, Paasivirta J (2000) Degradation half-life times of PCDDs, PCDFs and PCBs for environmental fate modeling. Chemosphere 40:943–949
20. Devi NL, Yadav IC, Shihua Q, Chakraborty P, Dan Y (2014) Distribution and risk assessment of polychlorinated biphenyls (PCBs) in the remote air and soil of Manipur, India. Environ Earth Sci 72:3955–3967
21. Kannan K, Blankenship AL, Jones PD, Giesy JP (2000) Toxicity reference values for the toxic effects of polychlorinated biphenyls to aquatic mammals. Hum Ecol Risk Assess 6:181–201
22. Qiao M, Chen Y, Wang CX, Wang Z, Zhu YG (2007) DNA damage and repair process in earthworm after in vivo and in vitro exposure to soils irrigated by wastewaters. Environ Pollut 148:141–147
23. Shin SK, Kim TS (2006) Levels of polychlorinated biphenyls (PCBs) in transformer oils from Korea. J Hazard Mater 137:1514–1522
24. Buekens A, Stiegitz L, Hell K, Huang H, Segers P (2001) Dioxins from thermal and metallurgical processes: recent studies for the iron and steel industry. Chemosphere 42:729–735