

Monitoring and risk assessment of polychlorinated biphenyls (PCBs) in agricultural soil collected in the vicinity of an industrialized area

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Abstract Samples of agricultural soils possibly contaminated by polychlorinated biphenyls (PCBs) were collected from Anseong, Korea. The agricultural areas chosen have possibly been contaminated by nearby factories, either directly or via atmospheric deposition, and require monitoring. The concentrations of 29 out of 209 PCB congeners were determined at five sites using high-resolution gas chromatography/high-resolution mass spectrometry. Total concentrations of the 29 PCB congeners in soil samples obtained from each study site were 106.65, 149.15, 222.67, 166.15, and 118.28 $\mu\text{g g}^{-1}$ dry weight, respectively, with pentaCBs and hexaCBs giving the highest concentrations of the congeners studied. The total toxic equivalent (TEQ) for 12 PCBs from each site was 0.05, 0.11, 0.08, 0.05, and 0.04 ng kg^{-1} dry weight, respectively. These values were mainly due to high TEQ values for PCB 126 (3,3',4,4',5-pentachlorobiphenyl)

from each site (at 0.05, 0.10, 0.07, 0.04, and 0.03 ng kg^{-1} dry weight, respectively). The TEQ values are much lower than the action level of 20 $\text{ng WHO-TEQ kg}^{-1}$ recommended by the World Health Organization, but PCB concentrations in this area should be monitored nonetheless, since these man-made compounds bioaccumulate, thus threatening the ecosystem and human health.

Keywords Gas chromatography/high-resolution mass spectrometry · Monitoring · Polychlorinated biphenyls · Toxic equivalent

Introduction

Polychlorinated biphenyls (PCBs) are still classified as one of the major contaminants around the world due to their high persistence, toxicity, and bioaccumulative properties, and was defined as persistent organic pollutants (POPs) by the Stockholm Convention (Stockholm Convention 2008). The manufacture, processing, and distribution of PCBs were prohibited in most nations in the late 1970s. Mixtures of PCB congeners, first manufactured by Monsanto Corporation (an American company) in 1929 (Barbalace 2003), were used for a wide range of industrial purposes (i.e., in transformer oil and capacitors) up until the late 1970s. However, many studies report that manmade PCBs continue to be widely distributed in the environment through the food chain, since they do not easily break down and thus bioaccumulate in living organisms. In addition, existing products and equipment containing PCBs, such as transformer oil, paints, adhesives, and fire retardant hydraulic systems, are still in use (ATSDR 2000). The continued use of these products results in increased risk of PCB contamination for years to come since they are not

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readily degrade biologically, physically, and chemically (ATSDR 2000).

The worldwide distribution of PCBs was exhaustively studied (Beyer and Biziuk 2009). Exposure to high levels of PCBs had a negative effect on human health and threatened the ecosystem (ATSDR 2000; WHO 2000). Since the lipophilic property of PCBs allows the compounds to persist in the fat tissues of humans and animals, they can have harmful effects on long-lived species, in particular humans, turtles, and other amniotes (Ming-ch'eng Adams et al. 2016). PCBs are also known to cause endocrine disruption and cancer, and to increase the risk of fetal developmental problems if ingested during pregnancy (Ming-ch'eng Adams et al. 2016).

In Korea, PCBs are still found in soil, sediment, and agricultural water collected near industrial areas in Gyeonggi, Daejeon, and Gyeongsang provinces. Several studies on PCB distribution in sediment, water, and soil in Masan and Gyeonggi Bay have been carried out (EPA 2000; Lee et al. 2001; Hong et al. 2006, 2010). Hong and coworkers reported that the average total concentration of 22 PCBs from 21 sites was 7.2 and 4.2 ng g⁻¹ dry weight in surface and core sediments, respectively. It was also suggested that PCB contamination was attributed to shipping and other industrial activities (Hong et al. 2010).

The current study aimed to determine concentrations of PCBs (using 29 out of 209 congeners) in soil collected from an agricultural area near a transformer oil manufacturer in Anseong, Korea using high-resolution gas chromatography/high-resolution mass spectrometry. This current study also aimed to provide a foundation for monitoring the distribution of PCBs in the study area by obtaining toxicity equivalency values of specific PCB congeners.

Materials and methods

Sample preparation

Soil samples were collected at five sites (5–15 cm, surface soil) in Anseong, Gyeonggi, Republic of Korea (site 1: 37°0'20"N 127°17'26"E, site 2: 37°0'9"N 127°17'38"E, site 3: 37°0'30"N 127°17'50"E, site 4: 37°0'24"N 127°17'1"E, and site 5: 37°28'59"N 127°58'18"E). The soil samples collected from the field were dried at the room temperature and passed through a 2-mm sieve. Soxhlet extraction was performed on 10 g soil samples mixed with 40 g of sodium sulfate and surrogate standards (68B-LCS, Wellington Laboratories, Guelph, Ontario, Canada). The Soxhlet extraction was run with 300 mL of dichloromethane for 24 h. The extracts were then concentrated and exchanged into *n*-hexane. For cleanup, the extracts

were eluted with *n*-hexane (150 mL) on multi-layer silica gel (Silica gel 60, Merck, Germany) columns—from bottom to top: activated silica gel (0.9 g), 3 g of basic silica gel (2 % KOH), silica gel (0.9 g), 4.5 g of acidic silica gel (44 % H₂SO₄), acidic silica gel (22 % H₂SO₄) (6 g), activated silica gel (0.9 g), silver nitrate silica gel (10 % of AgNO₃) (3 g), and sodium sulfate (6 g). The eluate was evaporated under a rotary evaporator and a gentle stream of nitrogen and then exchanged into nonane. The final solvent was concentrated to 50 μL prior to the instrumental analysis. Internal standards (68B-IS, Wellington Laboratories) were added to GC insert vials before GC injection.

Instrumental analysis and QA/QC

A gas chromatograph (Agilent Technologies 7890A, Santa Clara, CA, USA) coupled with a high-resolution mass spectrometer (Waters Autospec PremierTM, UK) was used for sample analysis. With the electron-impact ionization mode, mass spectra were obtained by 35 eV. The target analytes were separated on a non-polar capillary column (DB-5MS, 50 m × 0.25 mm i.d × 0.25 μm film thickness, Agilent Technologies). The initial oven temperature was set at 90 °C (held for 1 min), ramped into 170 °C at 20 °C min⁻¹ (held for 4 min), ramped into 280 °C at 3.5 °C min⁻¹, and lastly ramped into 320 °C at 50 °C min⁻¹ (held for 8.77 min). Data were recorded in the selected ion monitoring mode. The HRMS system was operated in a resolution of 10,000. The final sample (1 μL) was injected into GC in splitless mode. The carrier gas was helium (He) and flow rate was at 1 mL min⁻¹.

PCBs was identified based on the criteria reported by the US-EPA (method 1668C), and quantified by the isotope dilution method using calibration standards (EC9605-CVS and 68C-CVS, Wellington Laboratories). Target compounds were the 29 PCBs with IUPAC numbers of 18, 28, 33, 44, 52, 70, 77, 81, 101, 105, 114, 118, 123, 126, 128, 138, 153, 156, 157, 167, 169, 170, 180, 187, 189, 194, 195, 199, and 206. The recovery ratios of the surrogate standards ranged from 62.2 to 110.8 %.

Calculation for toxic equivalency quantities (TEQ)

The toxic equivalency factor (TEF) system was introduced to facilitate risk assessment of various classes of toxic chemical mixtures (i.e., dioxin-like chemicals or PCB congeners) and has been used by a wide range of studies. The overall toxicity—*toxic equivalents (TEQ)*—of a mixture is described by the addition of the concentrations of each compound (*C_i*) multiplied by its relative toxicity (TEF_{*i*}) (Safe 1998).

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

Results and discussion

Total concentration of PCBs

Monsanto corporation produced more than 90 % of PCBs globally, and its products were traded under the brand name of Aroclor, consisting of a various mixture of individual PCB congeners (Ivanov and Sandell 1992). In the current experiment, the concentration of 29 PCB congeners was determined in soil samples obtained for risk assessment purposes. Table 1 lists the concentrations of PCBs found at each of the five sites. The total concentration of all 29 PCB congeners analyzed was 106.65, 149.15, 222.67, 166.15, and 118.28 pg g^{-1} dry weight at each site, respectively. Total concentrations of pentaCBs and hexaCBs were the highest out of the seven homologs at all of the sites analyzed (Fig. 1). It should be noted that some

pentaCBs (PCB 105, 114, 118, and 123) and hexaCBs (PCB 156, 157, and 167) were designated by the World Health Organization (WHO) in 1998, since they are known to be particularly toxic to human health and the ecosystem (Van den Berg et al. 1998).

Toxic equivalency quantities (TEQ) of 12 PCBs

TEF expresses the toxicity of polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans, and PCBs in respect of the most toxic form of dioxin, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD); the toxicity of each compound may be different by orders of magnitude. TEF values were assigned to the 12 PCB congeners (Table 2) designated by WHO as most like TCDD (Van den Berg et al. 1998). The TEF values of

Table 1 Concentration of each PCB congener analyzed in soil samples from five different sites in Anseong, Gyeonggi Province

Compounds (IUPAC no.)	PCBs concentration (pg g^{-1}) in each site				
	1	2	3	4	5
2,2',5-TriCB (18)	2.77	4.73	3.83	0.43	0.64
2,4,4'-TriCB (28)	7.26	20.28	18.02	0.22	0.00
2',3,4-TriCB (33)	1.94	4.22	4.25	0.06	0.00
2,2',3,5'-TetraCB (44)	2.60	3.70	7.29	2.18	0.96
2,2',5,5'-TetraCB (52)	5.65	9.54	13.22	4.93	0.40
2,3',4',5-TetraCB (70)	5.77	11.13	14.51	6.32	5.10
3,3',4,4'-TetraCB (77)	0.97	2.14	2.72	1.76	0.48
3,4,4',5-TetraCB (81)	0.18	0.46	0.42	0.12	0.11
2,2',4,5,5'-PentaCB (101)	9.19	13.81	23.74	13.13	10.47
2,3,3',4,4'-PentaCB (105)	4.95	5.40	8.59	8.78	9.86
2,3,4,4',5-PentaCB (114)	0.51	0.63	0.20	0.62	0.54
2,3',4,4',5-PentaCB (118)	10.71	11.98	19.26	17.34	18.97
2',3,4,4',5-PentaCB (123)	0.56	0.55	0.59	0.74	0.58
3,3',4,4',5-PentaCB (126)	0.50	0.97	0.69	0.42	0.30
2,2',3,3',4,4'-HexaCB (128)	3.79	3.70	6.61	7.08	5.42
2,2',3,4,4',5'-HexaCB (138)	16.86	15.10	32.50	31.80	22.95
2,2',4,4',5,5'-HexaCB (153)	13.74	15.19	25.70	25.20	17.96
2,3,3',4,4',5-HexaCB (156)	1.68	2.06	3.18	2.99	2.34
2,3,3',4,4',5'-HexaCB (157)	0.53	0.53	0.97	0.73	0.58
2,3',4,4',5,5'-HexaCB (167)	0.69	0.90	1.27	1.67	1.33
3,3',4,4',5,5'-HexaCB (169)	0.00	0.46	0.29	0.11	0.12
2,2',3,3',4,4',5-HeptaCB (170)	3.66	4.25	6.28	7.63	4.04
2,2',3,4,4',5,5'-HeptaCB (180)	6.13	6.67	12.09	14.36	6.43
2,2',3,4',5,5',6-HeptaCB (187)	2.67	3.96	6.90	7.82	3.46
2,3,3',4,4',5,5'-HeptaCB (189)	0.34	0.52	0.44	0.45	0.29
2,2',3,3',4,4',5,5'-OctaCB (194)	0.71	1.45	1.80	1.94	1.08
2,2',3,3',4,4',5,6-OctaCB (195)	0.39	0.67	0.94	1.08	0.56
2,2',3,3',4,5,6,6'-OctaCB (199)	1.09	2.42	3.30	3.39	1.65
2,2',3,3',4,4',5,5',6-NonaCB (206)	0.82	1.73	3.06	2.82	1.66
Total	106.65	149.15	222.67	166.15	118.28

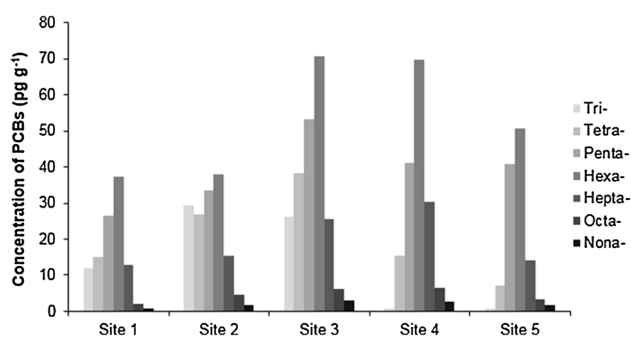


Fig. 1 Concentrations of each PCB homolog (classified by the number of chlorines attached to the aromatic rings) from each site

the 12 PCB congeners were reevaluated by WHO, with values now ranging from 0.00001 to 0.1 (Van den Berg et al. 2006).

The TEQ values for this experiment were obtained by multiplying concentrations for each of the 12 indicated PCBs by their assigned TEF values, and the results added up for a total value. Resulting total TEQ was 0.05, 0.11, 0.08, 0.05, and 0.04 ng kg⁻¹ dry weight at each site, respectively, which is much lower than the action level of 20 ng WHO-TEQ kg⁻¹ (Andersson et al. 2011). However, it should be noted that these values were mainly due to the TEQ values for PCB 126 (3,3',4,4',5-pentachlorobiphenyl), at 0.05, 0.10, 0.07, 0.04, and 0.03 ng kg⁻¹ dry weight for each site, respectively (Table 2). The TEF value for PCB 126 is also the highest (0.1) of the PCB congeners, meaning that PCB 126 is the strongest dioxin-like compound. Several studies on the toxicity of PCB 126 have been carried out (Lind et al. 2004; Zhang et al. 2012;

Shimada et al. 2015). Lind et al. demonstrated that female rats being exposed to PCB 126 exhibited increases in vascular risk factors, including serum cholesterol and blood pressure (Lind et al. 2004). PCB 126 was assessed if it directly had an effect on hepatic glucose metabolism with mouse hepatocytes (Zhang et al. 2012), with results demonstrating that aryl hydrocarbon receptor activation mediates dioxin-like PCB suppression of phosphoenolpyruvate carboxykinase expression, indicating that PCBs can act as energy metabolism disruptors. The new mechanism developed by Shimada et al. demonstrated that PCB 126 exposure impairs ex vivo G protein-coupled receptor pathway activation in innate immune cells, which may lead to a deficient immune defence in the host (Shimada et al. 2015).

Based on these results, the soil samples from Anseong are likely to be toxic to soil organisms due to the presence of the 12 dioxin-like PCB congeners. Therefore, further toxicity assessment of the agricultural areas in Anseong is strongly recommended, with a focus on concentrations of dioxin-like compounds (other than PCBs) designated by WHO. The combined results can then be used to complete a definite risk assessment, and appropriate monitoring programs can be implemented.

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Compliance with ethical standards

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

Table 2 The toxic equivalency quantities (TEQ) of 12 PCBs that were identified and determined in soil samples collected from Anseong, Korea

Congener (IUPAC no)	TEQ (pg kg ⁻¹) for each site				
	1	2	3	4	5
<i>Non-ortho-substituted PCBs</i>					
3,3',4,4'-TetraCB (77)	0.10	0.21	0.27	0.18	0.05
3,4,4',5-TetraCB (81)	0.06	0.14	0.13	0.04	0.03
3,3',4,4',5-PentaCB (126)	49.56	96.52	69.02	42.12	29.78
3,3',4,4',5,5'-HexaCB (169)	0.00	13.94	8.63	3.40	3.73
<i>Mono-ortho-substituted PCBs</i>					
2,3,3',4,4'-PentaCB (105)	0.15	0.16	0.26	0.26	0.30
2,3,4,4',5-PentaCB (114)	0.02	0.02	0.01	0.02	0.02
2,3',4,4',5-PentaCB (118)	0.32	0.36	0.58	0.52	0.57
2',3,4,4',5-PentaCB (123)	0.02	0.02	0.02	0.02	0.02
2,3,3',4,4',5-HexaCB (156)	0.05	0.06	0.10	0.09	0.07
2,3,3',4,4',5'-HexaCB (157)	0.02	0.02	0.03	0.02	0.02
2,3',4,4',5,5'-HexaCB (167)	0.02	0.03	0.04	0.05	0.04
2,3,3',4,4',5,5'-HeptaCB (189)	0.01	0.02	0.01	0.01	0.01
Total	50.00	110.00	80.00	50.00	30.00

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