



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



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HIGHLIGHTS

- Indicator PCBs in soil collected at 25 sites in Ulsan, South Korea were analyzed.
- The soils in Ulsan were slightly or moderately contaminated with indicator PCBs.
- The PCB levels at industrial and urban sites were higher than those at rural sites.
- Leakage from transformer oils appeared to be the main PCB source in major industries.
- PCB-containing paints were a major source for automobile and shipbuilding industries.

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ABSTRACT

The concentrations, profiles, and source-receptor relationships of seven indicator polychlorinated biphenyls (PCBs) (#28, 52, 101, 118, 138, 153, and 180) found in soil at 25 rural, urban, and industrial sites in Ulsan, South Korea were investigated. For this study, 75 soil samples were collected, 25 each in January of 2011, 2012, and 2013. Principal component analysis was used to evaluate the influence of the emission sources on the soil samples. The concentrations of total seven PCBs (Σ_7 PCBs) ranged between 0.034 ng/g and 143 ng/g (mean: 5.10 ng/g, median: 0.440 ng/g), which indicated slight or moderate contamination levels, respectively, compared to those in the other countries or other cities in Korea. The concentrations of Σ_7 PCBs at the industrial and urban sites were significantly higher than those at the rural sites, due to the direct influence of emission sources related to industrial activities rather than urban emission sources. Generally, the profiles of PCBs were dominated by penta- and hexa-chlorinated biphenyls at all the study sites, suggesting common sources of PCBs in Ulsan. PCB source identification indicated that leakage from transformer oils in the major industrial complexes and PCB-containing paints used in the automobile and shipbuilding industrial complexes were possibly the main sources of indicator PCBs in the study areas.

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1. Introduction

Polychlorinated biphenyls (PCBs) are a class of persistent organic pollutants (POPs) consisting of 209 congeners (IARC, 2015) that had been synthesized and produced as industrial chemicals from 1930 to 1993 (Breivik et al., 2002). Due to their beneficial

properties of thermal stability (UNEP, 1999) and resistance to both acids and alkalis (Bozlaker et al., 2008), PCBs have been used widely for industrial purposes (UNEP, 1999), such as in lubricating and hydraulic oils (Kalmaz and Kalmaz, 1979), heat transfer fluids in capacitors and transformers (Harrad et al., 1994), plastics additives (Hong et al., 2005), and plasticizers (Park et al., 2009). PCBs are unintentionally produced in chemical processes containing chlorine and hydrocarbon under high temperature (Breivik et al., 2004). Such processes include ferrous production, waste incineration, fuel combustion, and mineral production (Kim et al., 2007). After being

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emitted, PCBs can remain in the environment for a long time owing to the stability resulting from their physicochemical characteristics. Therefore, they are still found in various environmental media including soil (Armitage et al., 2006; Melnyk et al., 2015), sediment (Vane et al., 2007; Hong et al., 2010), atmosphere (Choi et al., 2008; Baek et al., 2010), and water (Harrad et al., 1994). PCBs are also detected in biota (Park et al., 2010; Lee et al., 2015) and humans (Moon et al., 2012). Because of their long residence time, wide distribution, bioaccumulation, and serious health influence (IARC, 2015), such as endocrine disruption, cancer development, and reproductive deficiency (WHO, 2003), PCBs were listed as POPs in the Stockholm Convention and have become one of the most concerning pollutants globally.

Generally, soil is regarded as a major reservoir of PCBs because of its high sorption capacity for organic contaminants (Meijer et al., 2003; Wu et al., 2011; IARC, 2015). In particular, when PCBs are emitted into the soil, they strongly bind to soil organic carbon and remain for a long time (Kukharchyk et al., 2007). In addition, due to their lipophilic nature, they can bioaccumulate in living organisms and then be transferred into food chains (Zheng et al., 2012). The PCBs in soil are derived mostly from dry/wet atmospheric deposition (Motelay-Massei et al., 2004; Bozlaker et al., 2008) and leakage of PCB-containing equipment (Harrad et al., 1994). Volatilization is a major route for transferring PCBs from soil to the atmosphere (Cetin et al., 2007). Because light PCBs (i.e., mono-, di-, tri-, and tetra-chlorinated biphenyls (CBs)) are more volatile than heavy ones (Strek and Weber, 1982), the light PCBs can be released more quickly from the soil, and their concentrations have been found to be lower than those of the heavy congeners.

Most of the PCBs intentionally produced (also known as commercial PCBs) were used as dielectric fluids for transformers and capacitors (UNEP, 1999). PCBs were never produced in Korea, but approximately 2900–6400 tons of PCBs were imported from the USA and Japan from the 1940s–1980s (Breivik et al., 2002; Shin and Kim, 2006). Since 1996, PCB concentrations higher than 50 ppm (mg/kg) have been banned from manufacture, import, and use as a nonfood additive agent in Korea (Kim et al., 2007). Moreover, as a signatory nation of the Stockholm Convention, Korea has made efforts toward removing PCBs (i.e., a decrease in use of products containing PCBs). For instance, the Ministry of Environment reached an agreement with national power companies with regard to PCB elimination in transformer oils by 2015 (Kim et al., 2007).

Leakage from transformers or capacitors is a major contributor to the soil contamination with the PCBs intentionally produced (Harrad et al., 1994). In Korea, 1.7 million transformers and 540 capacitors have been used to produce electricity (Kim et al., 2007). Among them, PCB concentrations higher than 2 ppm (mg/kg) and 50 ppm were found in 272 and 19 transformer oils, respectively (Kim et al., 2007). Therefore, this electrical equipment is an important PCB emission source in Korea because PCBs are likely to be released when this equipment is used, disposed of, or recycled. Industrial activities were also identified as a major source of PCBs in Korea. For instance, unintentionally produced PCBs could be released from the thermal processes of steel production (Choi et al., 2008; Baek et al., 2010; Fang et al., 2012) and fuel combustion (Kim et al., 2007). Additionally, shipbuilding activities in industrialized bays of Korea were noted as a source of PCBs because commercial PCBs occasionally were used in ship paints as additives (Hong et al., 2005).

The predominant industrial activities in Ulsan (an industrial capital in South Korea) include petrochemical, chemical, automobile, and ship production. To the best of our knowledge, few studies have focused on soil contaminated by PCBs in Ulsan. Most of the previous studies investigated PCB contamination in the sediment (Choi et al., 2001; Khim et al., 2001; Hong et al., 2005; Moon et al.,

2008) and atmosphere (Shin et al., 2011; Hogarh et al., 2012), indicating that PCB contamination in Ulsan was associated mostly with activities from the shipbuilding industrial complex (Khim et al., 2001; Hong et al., 2005). However, the other industrial activities in Ulsan (e.g., petrochemical and chemical processes) could be important sources of PCBs as well (Lee et al., 1996; Schuhmacher et al., 2004) due to their high-temperature production processes or spillage from PCB-containing equipment. In this study, soil samples were collected in Ulsan to investigate the concentrations and profiles of seven indicator PCBs. Based on these data, the spatial distribution and source-receptor relationships of PCBs were studied.

2. Materials and methods

2.1. Soil sampling method

Each January for three consecutive years (2011, 2012, and 2013), surface soil samples were collected at 25 sites in rural, urban, and industrial areas of Ulsan, Korea, for a total of 75. The sampling sites were selected based on our previous study (Kwon and Choi, 2014) and classified into three groups: rural (R1–R5), urban (U1–U10), and industrial (I1–I10) sites (Fig. 1). As there are several major industrial activities in Ulsan, the soil samples in the industrial areas were collected corresponding to these activities: non-ferrous industrial (I1–I4), petrochemical (I5–I8), automobile (I9), and shipbuilding/heavy industrial complexes (I10). At each sampling site, five sub-soil samples (5 m apart from each other, at a depth of 5 cm from the soil surface) were collected and mixed together for one final composite sample. The soil samples were then stored at -4°C until analysis.

2.2. Instrumental analysis and QA/QC

The target compounds of this study were seven indicator PCBs (#28, 52, 101, 118, 138, 153, and 180) that were predominant in commercial PCB mixtures (Harrad et al., 1994) and are still ubiquitous in the environment. Thus, such PCB congeners can act as possible representatives for all PCBs in the environment (Hodak Kobasic et al., 2015).

The soil samples were air dried at room temperature (23°C) and passed through a sieve (2 mm) to remove large particles. The homogenized samples (20 g) were mixed with diatomaceous earth and then extracted by an accelerated solvent extractor (ASE 350, Dionex, USA) using methylene chloride under 2000 psi at 140°C . The extraction was conducted in three cycles with 5 min heating, followed by 5 min static extraction. Prior to extraction, as a surrogate standard, PCB-209 (AccuStandard, USA) was added to the samples. After the extraction step, the extracts were evaporated using a Turbo VAP LV (Caliper, Life Sciences, USA), then cleaned up on a multilayer silica gel column consisting of sodium sulfate, activated silica gel (2 h at 600°C), 2% potassium hydroxide silica gel, 44% sulfuric acid silica gel, 22% sulfuric acid silica gel, and 10% silver nitrate silica gel. The extract was eluted with 200 mL hexane and evaporated with a nitrogen evaporator (Eyela MG-2200, Japan) to 0.5 mL, and then transferred to a gas chromatography (GC) vial. As an internal standard, 2,4,5,6-tetrachloro-meta-xylene (TCMX) was added to the sample before GC injection.

The processed samples were analyzed by a gas chromatograph (GC, Agilent 7890A, USA) coupled with a high-resolution mass spectrometer (HRMS, AutoSpec Premier, Waters, USA). The target analytes were separated on a DB5-MS column ($50\text{ m} \times 0.25\text{ mm i.d.} \times 0.25\text{ }\mu\text{m d}_f$). Each processed sample (1 μL) was injected into the GC in splitless mode at an injection temperature of 300°C . The carrier gas was helium (He) with a constant flow rate of 1.1 mL/min. The temperature of the GC oven was adjusted as follows: initially

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