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Severe pollution of PCDD/Fs and dioxin-like PCBs in sediments from Lake Shihwa, Korea: Tracking the source

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ABSTRACT

Concentrations of polychlorinated dibenzo-*p*-dioxins, dibenzofurans (PCDD/Fs) and dioxin-like polychlorinated biphenyls (DL-PCBs) were determined in surface sediments from Lake Shihwa and from creeks that discharge into this artificial lake. The toxic equivalents (TEQs) in sediments ranged from 1.0 to 1770 pg/g dry weight, which were some of the highest values ever reported so far for coastal sediments on a global basis. The concentrations of PCDD/Fs and DL-PCBs decreased with increasing distance from the creeks to offshore regions of the lake. Based on a multivariate statistical analysis and congener profiles, it was found that high contamination by PCDD/Fs in creek sediments collected around Lake Shihwa was associated with releases from chlor-alkali processes. Significant correlations were found for total organic carbon content and the concentrations of highly chlorinated PCDD/F congeners. This is the first report to document chlor-alkali processes as a significant source of PCDD/F contamination in Korean coastal waters.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) are widespread contaminants in the environment. PCDD/Fs and dioxin-like PCBs (DL-PCBs) have received considerable attention due to their toxicity and bioaccumulation potentials (Van den Berg et al., 2006). PCDD/Fs and PCBs are released from waste incinerators, chemical industries, and wastewater effluents (Moon et al., 2008a; Gidarakos et al., 2009; Li et al., 2012). According to a nationwide survey on the inventory of PCDD/Fs in Korea, the major sources of these compounds in the Korean environment were municipal solid waste incinerators (MSWIs) and steel industry, both collectively accounting for ~95% of the total emissions (NIER, 2009).

Lake Shihwa, an artificial saltwater lake (surface area = 56.5 km^2, drainage basin = 476.5 km^2), is located on the west coast of South Korea. The lake has well-developed tidal flats, which provide a habitat for aquatic animals and birds. The watershed of the Lake Shihwa region (total industrial area = 31 km^2) is characterized by one of most intensive industrial and urban development, in which more than 13,000 small- and large-scale industries produce metal products, machinery, equipments for industry and chemical products. The cities of Shiheung and Ansan (total population exceeding one million people) are located in the watershed of Lake Shihwa. Since several factories located in the Lake Shihwa region's industrial complex have been moved from the capital city (Seoul), one of the goals of the industrial the complex was to prevent environmental pollution (KICOX, 2011). However, rapid population growth and industrial development in this region has led to deterioration of water quality and biodiversity (Han and Park, 1999; D. Li et al., 2004; Rostkowski et al., 2006; Yoo et al., 2008).

The Korean government designated Lake Shihwa as a special management coastal zone and constructed a water gate in 2000 to promote water exchange with the adjacent Yellow Sea. However, several studies continue to report substantial contamination of Lake Shihwa water, sediment and biota by trace metals and toxic organic contaminants such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), perfluorinated compounds (PFCs), alkylphenols and polybrominated diphenyl ethers (PBDEs) (Khim et al., 1999; D. Li et al., 2004; Z. Li et al., 2004; Yoo et al., 2008, 2009; Oh et al., 2010; Choi et al., 2011; Ra et al., 2011; Moon et al., 2012). Despite several investigations on a variety of contaminants in the Lake Shihwa environment, little is known on PCDD/Fs and dioxin-like PCBs. In fact, very few studies have reported contamination and sources of PCDD/Fs and DL-PCBs in the coastal waters of Korea overall (Moon et al., 2008a,b, 2009; Hong et al., 2009). The objectives of this study were to investigate the contamination levels and sources of PCDD/Fs and DL-PCBs in sediments from Lake Shihwa, Korea.

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2. Materials and methods

2.1. Sample collection

The sampling locations of surface sediments (0–4 cm depth) from Lake Shihwa and surrounding creeks are shown in Fig. 1. Sediment samples were collected in March 2008, using a box core sampler in creeks (C1–C12), inshore (S1–S16) and offshore regions (SO1–SO6) of the lake. The samples were individually wrapped in clean aluminum foil, transported to a laboratory and freeze-dried.

2.2. Chemical analysis

Tetra- to octa-CDD/F homologues, 17 toxic 2, 3, 7, 8-substituted PCDD/F congeners, and 12 DL-PCB congeners (PCBs 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169 and 189) were analyzed in sediment samples. Detailed descriptions of extraction and cleanup procedures for sediment samples have been presented elsewhere (Moon et al., 2008a,b). In brief, sediments (about 10–20 g) were extracted in a Soxhlet apparatus using mixed solvents of dichloromethane (DCM; ultra residue analysis, J.T. Baker, Phillipsburg, NJ, USA) and hexane (ultra residue analysis, J.T. Baker) (3:1). Prior to extraction, PCB congeners 103, 198 and 209 were spiked into samples, as surrogate standards. The extract was divided into two portions prior to the purification for PCDD/Fs and DL-PCBs. The first aliquot (6 mL) was spiked with ^{13}C-labelled internal standards of PCDD/Fs (EPA-1613LCS; Wellington Laboratories, Guelph, ON, Canada) and the other aliquot (4 mL) was spiked with ^{13}C-labelled DL-PCBs (WP-LCS; Wellington Laboratories) for the quantification of PCDD/Fs and DL-PCBs, respectively. The aliquot for PCDD/F analysis was cleaned by passage through a multi-layer silica gel column (neutral, 70–230 mesh, Wako Pure Chemicals, Tokyo, Japan) with 200 mL of hexane (dioxin analysis grade, Wako Pure Chemicals) using the Dioxin Cleanup System (DAC695/DPU8; GL Sciences, Tokyo, Japan). The eluted fractions were purified on an activated alumina column using successive portions of 3% DCM in hexane and 50% DCM in hexane. The second fraction was used for the determination of PCDD/Fs. The aliquot for DL-PCBs was purified using only a multi-layer silica gel column.

2.3. Instrumental analysis and quality control

Identification and quantification of PCDD/Fs and DL-PCBs were performed using a high-resolution gas chromatograph interfaced with a high-resolution mass spectrometer (HRGC/HRMS; JMS 800D; JEOL, Tokyo, Japan). The details of the instrumental parameters have been reported elsewhere (Moon et al., 2008a,b). Briefly, PCDD/Fs and DL-PCBs were quantified using the isotope dilution method, based on relative response factors of individual congeners. The HRMS was operated in electron ionization mode, and ions were monitored by selected ion monitoring. A gas chromatographic column SP-2331 (60 m length, 0.25 mm inner diameter, 0.2 μm film thickness; Supelco, Bellefonte, PA, USA) was used for the separation of tetra- to hexa-CDD/Fs, and DB-5MS (60 m length, 0.25 mm inner diameter, 0.25 μm film thickness; J & W Scientific, Palo Alto, CA, USA) was used for the separation of hepta- to octa-CDD/Fs. DL-PCBs were analyzed using an HT-8 capillary column (50 m length, 0.22 mm inner diameter, 0.25 μm film thickness; SGE, Ringwood, VIC, Australia).

Solvents injected before and after the injection of the standards showed negligible contamination or carryover. Procedural blanks ($n = 6$) were processed in the same way as the samples and were

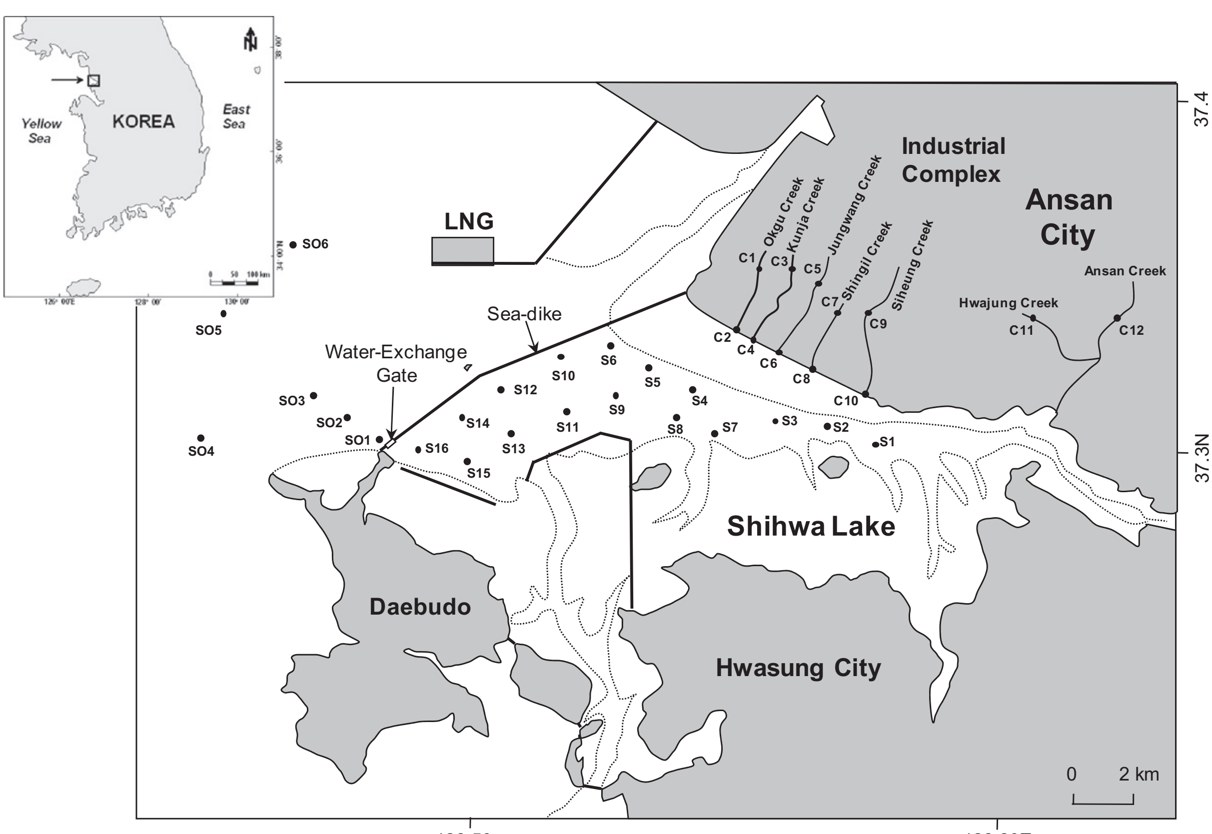

Fig. 1. Map showing the sampling locations of sediment from Lake Shihwa and its surrounding creeks, Korea. C1–C12 are the sampling locations from creeks. S1–S16 and SO1–SO6 are the sampling locations from inshore and offshore regions of the lake, respectively.