Chemosphere 184 (2017) 832–840

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Historical record of polychlorinated biphenyls (PCBs) and special occurrence of PCB 209 in a shallow fresh-water lake from eastern China

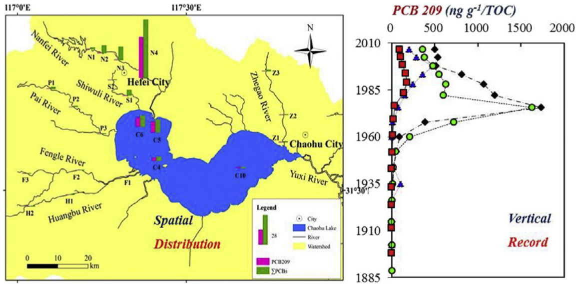
Shouliang Huo [a], Chaocan Li [a, *], Beidou Xi [a, **], Zhiqiang Yu [b], Kevin M. Yeager [c], Fengchang Wu [a]

[a] *State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Science, Beijing 100012, PR China*
[b] *Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, PR China*
[c] *Department Earth and Environmental Sciences, University of Kentucky, Lexington, KY 40506, USA*

HIGHLIGHTS

- ∑PCBs records are coincident with the enhancement of anthropogenic activities.
- PCB209 has been the predominant pollutants in sediments since the 1950s.
- Transformation of dominant congeners suggests a switch of local sources.
- PCB209 should be resulted from pigment synthetizing process in Heifei City.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 19 January 2017
Received in revised form
6 June 2017
Accepted 17 June 2017
Available online 18 June 2017

Handling Editor: Andreas Sjodin

Keywords:
Polychlorinated biphenyl
Historical record
PCB209 flux
Source apportionment

ABSTRACT

Concentrations of polychlorinated biphenyls (PCBs) were measured in dated sediment cores collected from the fifth largest freshwater lake in China, Lake Chaohu, to investigate PCB temporal trends, accumulation, and environmental fate. Total PCB concentrations in Lake Choahu sediments ranged from 0.03 to 24.11 ng g^{-1} (d.w.). PCB 209 was the dominant congener, accounting for 45.5%–83.9% of total PCBs detected after the mid-20th century. All PCB congeners were positively correlated with total organic carbon (TOC) concentrations. TOC-normalized PCB concentrations exhibited three stages of variation over time: a slight increase from their emergence in the early 20th century, followed by a rapid increase since the late 1950s (peaking in the late 1980s), before a general decrease to the present. Both compositional PCB patterns and principal component analysis (PCA) indicated a source switch from commercial PCBs to other sources. Major contributions of PCB209 to total PCBs in Lake Chaohu sediments is a highlight of this study, with results showing that PCB209 was derived from the upstream city of Hefei, and the production of phthalocyanine-type pigments is the likely source of PCB209.

1. Introduction

Polychlorinated biphenyls (PCBs) were widely used for decades in electrical transformers and capacitors as insulation oil all over the world. Though the production and use of PCBs ceased decades

---

* Corresponding author.
** Corresponding author.
E-mail address: liccann@126.com (C. Li).

http://dx.doi.org/10.1016/j.chemosphere.2017.06.073

ago due to their persistent and toxic character, PCBs are still detected in many different environments (Marek et al., 2014; Combi et al., 2016; Liu et al., 2015; Naffrechoux et al., 2015). Sediments are major reserviors for PCBs (Yuan et al., 2001; Rabodonirina et al., 2015), and the presence of these toxic compounds in sediments can disturb aquatic ecosystems, endanger bottom-dwelling organisms (benthos, demersal fish), and these sediments can also serve as important secondary sources of PCBs (Weber and Goerke, 2003; Kannan et al., 2005). Thus, studies of PCB accumulation in sediments are necessary to quantify current pollution status and PCB transportation mechanisms (Kim et al., 2008). PCB records in well-dated sediment cores can provide effective data sets for reconstructing historical pollution records (Brenner et al., 2004; Schmid et al., 2010; Martinez and Hornbuckle, 2011). To determine how anthropogenic processes and sedimentological variability affect the transport of PCBs, we focus on the contamination status of PCBs in the fifth largest freshwater lake in China, Lake Chaohu. This research is important because Lake Chaohu functions as an important water resource for eastern China, and studies on PCBs contamination in Lake Chaohu are limited (Tremolada et al., 2015; Turrio-Baldassarri et al., 2007).

Trichlorobiphenyl (#1 PCB) and pentachlorobiphenyl (#2 PCB) are well known PCB commercial products produced in China, whose chlorine proportions are similar to Aroclor 1242 and 1254, respectively (Ren et al., 2007). Imported electrical capacitors and E-wastes from abroad have also brought a variety of Aroclor-containing materials to China. Thus, sources of PCB congeners in China can be estimated using the congener composition of Aroclors as “fingerprints” for source apportionment (Wyrzykowska et al., 2006; Yang et al., 2009). Di-to hexa-PCBs are frequently detected congeners, which can be attributed to certain PCB sources (Wyrzykowska et al., 2006). However, some unintentionally-produced PCB emissions from industrial processes are also important sources (Duan et al., 2013; Hong et al., 2005; Liu et al., 2009), and meanwhile limited suties are related to the highly chlorinated PCBs, especially deca-PCBs (Howell et al., 2008; Koh et al., 2015). Therefore, identifying specific sources for PCBs, especially for the highly chlorinated PCBs (such as deca- PCB and nona- PCBs), remains difficult.

In this study, we analyzed the historical record of PCBs, including deca-PCB, in sediment from Lake Chaohu, in order to achieve the following objectives: (1) to reconstruct the timing, types and severity of historical pollution of PCBs, (2) to investigate the relationship between the human activities and variability in PCB contamination, and (3) to determine possible sources of highly chlorinated PCBs.

2. Materials and methods

2.1. Study area and sample collection

Lake Chaohu is a shallow, eutrophic lake located in eastern China between the Huaihe River watershed and the Yangtze River delta (117°16′-117°51′N, 31°25′-31°43′E). The lake has a surface area of 780 km^2, and is divided into two sections by Mushan Island, namely the western lake (ca. 1/3 of the lake area) and eastern lake (ca. 2/3 of the lake area). The western lake receives major inflows, including the Nanfei and Shiwuli Rivers (both have sewage outfalls), the Hangbu and Fengle Rivers, and the Pai River (which contributes the greatest discharge) (Fig. 1). These western rivers account for almost 60% of the total runoff volume contributed annually to the lake. The Yuxi River is the only channel connecting the eastern lake and the Yangtze River, permitting water exchange. Lake Chaohu has played a significant role in regional socioeconomic development, in terms of flood control, municipal water supply, crop irrigation, transportation, fisheries, and other valuable ecosystem services (Chen et al., 2011; Zhang et al., 2015). However, in recent decades, intense anthropogenic activities in the lake's watershed have resulted in serious industrial and domestic pollution of the lake. The primary rivers discharging into the lake carry considerable contaminant loads, as they pass through heavily urbanized, industrialized, and agriculturally utilized areas (Tang et al., 2010; Combi et al., 2013).

Four sediment cores were collected in July, 2011 from Lake Chaohu (Fig. 1). The sampling sites were chosen away from lake banks, stream inlets and the lake outlet to diminish any disturbance of the sediment by scouring or re-suspension. Two cores were collected near the estuary of the Nanfei and Shiwuli Rivers in the western lake (C5 and C6, respectively). The other two cores (C4 and C10) were collected from the centers of the western, and eastern lake, respectively. The sediment cores were collected using a gravity corer equipped with a PMMA (acrylic) tube, with an inner diameter of 8 cm, and length of 50 cm. Each core sample was vertically extruded, and horizontally sectioned at 2 cm intervals, resulting in a total of 25 sections per core. Additionally, four surface sediment samples were collected near to each of the core samples, and 18 surface sediment samples were collected along sections of the Zhegao, Nanfei, Shiwuli, Pai, Fengle and Huangbu Rivers using a stainless steel grab sampler (Fig. 1). After transport to the laboratory, all samples were freeze-dried, homogenized, sieved through a 100 mesh sieve, and stored at −20 °C until analysis.

2.2. Chemical analyses

Total organic carbon (TOC) of the sediment samples was determined using a TOC analyzer (MultiN/C2100, AnalytikJena AG, Germany) after acidification.

Sediment sample extraction and cleanup procedures have been described in detail previously (Li et al., 2015). In summary, about 10 g of freeze-dried sample was spiked with ^{13}C-labled PCB surrogate standards, and were soxhlet extracted for 48 h in dichloromethane solvent (200 ml). Sulfur was removed by activated copper. Extracts were then concentrated by a rotary evaporator, and the solvent was exchanged to hexane, and then purified using a combined glass column packed with 1:2 alumina/silica gel. After eluting aliphatic hydrocarbons with about 15 ml n-hexane, the PCB fraction was eluted with a mixture of 70 ml n-hexane:dichloromethane (7:3 by volume). The purified fraction was then concentrated to 0.2 ml under a gentle nitrogen stream. Internal standards were added before instrumental analysis.

A total of 41 individual PCB compounds (IUPAC No.: 17, 18, 28, 31, 33, 44, 49, 52, 70, 74, 82, 87, 95, 99, 101, 105, 110, 118, 128, 132, 138, 149, 151, 153, 156, 158, 169, 170, 171, 177, 180, 183, 187, 191, 194, 195, 199, 205, 206, 208 and 209), purchased from Accustandard Inc. (New Haven, CT. USA), were determined on an Agilent gas chromatograph, coupled to a tandem quadrupole mass spectrometer (Agilent 7980A/7000 GC-MS/MS triple quad), using a DB-5ms fused-silica capillary column (30 m × 0.25 mm i.d., 0.25 μm, J & W Scientific, USA). High purity He was the carrier gas, at a flow rate of 1 ml/min. The temperature of the injection port was set at 250 °C. The GC oven program was set as follows: starts at 80 °C and holds for 2 min; then raised to 160 °C at 10 °C/min.; then increased at 3 °C/min. to 250 °C, and afterwards with no hold to reach 290 °C at 10 °C/min. The ion source utilized electron impact ionization (EI), and multiple reaction monitoring was applied in qualitative and quantitative analyses. The injection port, transfer line, ion source, and quadrupole rods were at 250, 300, 230 and 150 °C, respectively. Helium and nitrogen were separately used as quench (2.25 mL/min) and collision (1.5 mL/min) gases.