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Occurrence, distribution and risk assessment of polychlorinated biphenyls and polybrominated diphenyl ethers in nine water sources

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ABSTRACT

Water quality of water sources is a critical issue for human health in South China, which experiences rapid economic development and is the most densely populated region in China. In this study, the pollution of organohalogen compounds in nine important water sources, South China was investigated. Twenty six organohalogen compounds including seventeen polychlorinated biphenyls (PCBs) and nine polybrominated diphenyl ethers (PBDEs) were detected using gas chromatograph analysis. The concentrations of total PCBs ranged from 0.93 to 13.07 ng L^{-1}, with an average value of 7.06 ng L^{-1}. The total concentrations of nine PBDE congeners were found in range not detected (nd) to 7.87 ng L^{-1} with an average value of 2.59 ng L^{-1}. Compositions of PCBs and PBDEs indicated the historical use of Aroclors 1248, 1254 and 1260, and commercial PBDEs may be the main source of organohalogen compounds in water sources in South China. The nine water sources could be classified into three clusters by self-organizing map neural network. Low halogenated PCBs and PBDEs showed similar distribution in the nine water sources. Cancer risks of PCBs and PBDEs via water consumption were all below 10^{-6}, indicating the water quality in the nine water sources, South China was safe for human drinking.

1. Introduction

Water quality issues are a major challenge for human health in the 21st century due to critical water shortage and pollution. Moreover, fresh water in China is under immense stress due to rapid population growth, urbanization and unsustainable consumption of water in industry and agriculture (Qu and Fan, 2010). Although, a great number of lakes and major rivers exist in China, only half of China's 200 major rivers and less than a quarter of its 28 major lakes and reservoirs are suitable for use as drinking water after treatment (Zhang et al., 2010). Most seriously, more than 300 million people rely on hazardous drinking water sources, which are contaminated with untreated sewage, industrial pollutants and agricultural chemicals (World Bank, 2007; Rong et al., 2009). Hence, nearly 11% of digestive cancer cases are related with chemical contaminants in drinking water worldwide (WHO-UNDP, 2001). However, organic chemicals of concern for protection of ecological and human health are less emphasized in the water quality assessment criteria. Organohalogen compounds in water are of great concern for human health due to their persistent, toxic and bioaccumulative nature (Daso et al., 2013; Hellar-Kihampa et al., 2013; Moon et al., 2012; Yang et al., 2013), such as polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs). PCBs have been manufactured and used largely worldwide, especially in the developing countries such as China, Malaysia, India, Kenya, and various African countries (Wong et al., 2007). PBDEs are the most commonly used reactive flame retardants and are structurally similar to PCBs (Alaee et al., 2003; Rahman et al., 2001). In China, since the production and use of PCBs were prohibited in 1990s, most of the outdated PCB-containing equipment (equipment filled with PCBs as dielectric fluid) was removed from use and stored (Xing et al., 2005). But, no bans or restrictions of PBDEs have been commenced in China (Liu et al., 2009).

Water environment has been considered as an important pool for the PCBs and PBDEs via a variety of routes, such as surface runoff and atmospheric deposition (Howell et al., 2008; Zhang et al., 2007). Once in the environment, PBDEs and PCBs can eventually accumulate in upper trophic level species via food chain, including marine mammals, some birds and fish, and humans (Brown et al., 2006). Eventually, PCBs and PBDEs may pose a great threat to ecosystem and human health. Hence, to understand the levels of PCBs and PBDEs in the water resources were very

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important for water management and human health.

South China covers Guangdong and Hainan provinces, Guangxi Zhuang Autonomous Region, Special Administrative Regions of Hong Kong and Macao, accounting for about 13% of total gross domestic product (GDP) in China. However, the region also experienced severe pollution of heavy metals and organic contaminants in the last three decades (Wang et al., 2013; Zhang et al., 2013b). The pollution of PCBs and PBDEs were more severe, especially in the Pearl River Delta (Chen et al., 2013; Zhang et al., 2013a; Zhang et al., 2013b). However, no study has focused on contamination of PCBs and PBDEs in drinking water sources in South China. Therefore, the main objective of this study was to investigate the pollution levels, distribution and risk assessment of PCBs and PBDEs in drinking water sources of South China, including Guangdong and Hainan provinces, and Guangxi Zhuang Autonomous Region.

2. Methods and materials

2.1. Chemicals and materials

Seventeen PCB congeners including Di-CB, Tri-CB, Tetra-CB, Penta-CB, Hexa-CB and Hepta-CB (IUPAC numbers: CB 8, 28, 30, 37, 44, 52, 77, 82, 87, 99, 101, 105, 114, 128, 156, 158, 179) were analyzed, in which CB 77, 105, 114 and 156 are dioxin-like congeners. Nine PBDEs (IUPAC numbers: BDE 28, 35, 47, 77, 99, 100, 153, 154, 183) were targeted for analysis as well in the study, which usually had high abundance in water and human tissues. Pure standards were purchased from AccuStandard Inc., USA and diluted to the working concentrations (5–100 μg L^{-1}). All organic solvents used for sample processing and analysis were HPLC grade (Fisher Scientific, USA).

2.2. Studied area and sample collection

To understand the present situation and distribution characteristics of PCBs and PBDEs in drinking water sources of the South China, water samples from nine water sources in Guangdong and Hainan provinces and Guangxi Zhuang Autonomous Region were collected in June 2013. The daily production of selected water sources were at least 100,000 m^3 day^{-1}. Detail information of sampling sites was presented in Fig. S1 (See supporting information). At each sampling sites, five surface water samples (0.5 L, 0–15 cm) were collected by hand using pre-cleaned PVC bottle and mixed as one sample (2.5 L). All the water samples were filtrated through 0.45 μm hydrophilic filters under vacuum to get rid of the particulates, followed by extraction of PCBs and PBDEs within 7 days.

2.3. Solid-phase extraction

The target PCBs and PBDEs in the surface water samples were extracted with BondEluent C18 500 mg cartridges (Aglient, USA) that were previously conditioned with dichloromethane (5 mL), water (5 mL) and methanol (5 mL). After loading of 1000 mL of water samples, the cartridges were dried for 15 min under vacuum. Then, the analytes were eluted with 15 mL of dichloromethane. After drying under a gentle stream of high purity nitrogen, the extracts were reconstituted with 100 μL of n-hexane for gas chromatographic (GC) analysis.

2.4. Chromatographic analysis

Qualitative and quantitative analysis of PCBs and PBDEs were analyzed with a GC–MS using electron-ionization ion source (EI) in the selected ion monitoring mode (Agilent GC 7890 coupled with 5975 MSD, Agilent Technologies, Santa Clara, CA, USA). A capillary column HP-5 (Agilent Technology, 30 m × 0.25 mm i.d. × 0.25 μm) was used for the separation of the PCBs and PBDEs. Helium gas was used as the carrier gas. The injection volume was 1 μL. Peaks generated by either the retention time or the mass detectors were identified by comparison with seventeen PCBs and nine PBDEs standards purchased from AccuStandard Inc., USA.

For PCBs analysis, the oven temperature started at 70 °C for 2 min, increased to 150 °C at a rate of 25 °C min^{-1}, then increased to 200 °C at a rate of 3 °C min^{-1} and finally increased to 280 °C at a rate of 8 °C min^{-1} and maintained the temperature 10 min. The flow rate of the carrier gas was set at 1.9 mL min^{-1}.

For PBDEs analysis, the oven temperature started at 110 °C for 2 min, increased to 200 °C at a rate of 40 °C min^{-1}, then increased to 260 °C for 1 min at a rate of 3 °C min^{-1} and finally increased to 280 °C for 2 min at a rate of 10 °C min^{-1}. The flow rate of the carrier gas was set at 1.2 mL min^{-1}.

2.5. Quality assurance and quality control (QA/QC)

All data were subject to strict quality control procedures. The recovery can be determined by division of the detected concentration of the organohalogen compounds and the known amount of organohalogen compounds spiked in water. The field blank was taken with HPLC grade water by simulating collection of field sample (Zhang et al., 2007). Average recoveries of the PCBs and PBDEs ranged from 70% to 115% for the water samples at the spiked concentration of 5 ng L^{-1}. Regular injections of field blanks, solvent blanks and standard solutions of target compounds were done before and during instrumental analyses to check for instrument's performance and cross contamination. PCBs and PBDEs were not detected in the field blanks. The limits of detection (LOD) of PCBs and PBDEs were defined as three times of the signal-to-noise ratio (S/N). The LOD of eight PCBs and PBDEs in this study were 0.03 to 0.15 ng L^{-1} depending on the degree of halogenation of different congeners. All the results were corrected with the recovery rates.

2.6. Self-organization map (SOM) neural network

Kohonen self-organization map (SOM) (Kohonen, 2001), an unsupervised artificial neural network, was widely used to classify the metal pollution (Alvarez-Guerra et al., 2008; Arias et al., 2008; Lee and Scholz, 2006). Also, the SOM is little affected from the size of data (Lee et al., 2002). The neurons of the output layer of SOM were arranged on a topological map, forming a two-dimensional lattice. The Kohonen training algorithm was devised to encourage the formation of clusters of similar cases at nearby positions in the lattice. Hence, samples within the same node could share the more similarities (Subida et al., 2013b). The aim of this neuronal tool used in this study was to discover similar patterns among the organohalogen compounds and water sources.

The PCB and PBDE congers were first classified into nine variables based on halogenated number of these compounds as follows: Di-CB, Tri-CB, Tetra-CB, Penta-CB, Hexa-CB, Hepta-CB, Tri-BDE, Tetra-BDE and Hexa-BDE. Then, the Nine variables used in the SOM were normalized by a log transformation. The topology of SOM obtained with different normalization method was selected based on the criteria of the quantization error (QE) and the topographic error (TE) (Subida et al., 2013a). QE, referred to the average distance between each data vector and its best matching unit, measured map resolution. TE, described the proportion of all data vectors for which first and second best matching units were not adjacent units, measured topology preservation. Finally, a 15-unit map (5 × 3) with low quantization error and the topographic