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Polybrominated diphenyl ethers and polychlorinated biphenyls in sediments of southwest Taiwan: Regional characteristics and potential sources

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ABSTRACT

Very little information is available on the contamination of coastal sediments of Taiwan by PBDEs and PCBs. In this study, we determined the concentrations of 19 PBDE and 209 PCB congeners in 57 surface sediment samples to identify the possible sources of PBDEs and PCBs. The total PBDE and PCB concentrations ranged from below detection limit to 7.73 ng/g and 0.88–7.13 ng/g, respectively; these values are within the ranges observed for most coastal sediments worldwide. The PBDE congeners were dominated by BDE-209 (50.7–99.7%), with minor contributions from penta- and octa-BDEs. The signatures of PCB congeners suggested that PCB residues in Kaohsiung coast may be the legacy of past use or the result of ongoing inputs from the maintenance, repair and salvage of old ships. Principal component analysis of the congener-specific composition of PBDEs and PCBs revealed distinct regional patterns that are related to the use of commercial products.

1. Introduction

Halogenated organic chemicals have been widely used for a variety of purposes since the beginning of the 20th century, and industrial production of these chemicals, including polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs), has been widespread for commercial purposes (Alaee et al., 2003; Van den Berg et al., 1998). The presence of these compounds in remote regions has provided evidence for their atmospheric and long-range dispersal (Ballschmiter et al., 2002), and based on scientific evidence several international agreements such as Stockholm convention and regulations have been established with the aim of restricting the use of these persistent organic pollutants.

The persistent, bio-accumulative and toxic nature of many organochlorine compounds, including PCBs, was discovered in the early 1960s (Bogdal et al., 2008). PCBs were widely used as dielectric fluids and insulators, and it has been estimated that more than 1.3 million tons were produced worldwide between 1929 and 1989 (Breivik et al., 2002). The high toxicity of PCBs was confirmed in the 1970s, and their production is now prohibited in most countries. However, many PCB-containing products manufactured prior to prohibition of their production are still in use or are in landfill sites, and can contaminate the environment by evaporation and leakage. Therefore, PCBs continue to be detected in the environment. To aid in the interpretation of their contamination into measures of adverse biological effects, sediment quality guidelines (SQGs) have been developed over 20 years. These guidelines have been demonstrated to be a useful tool for assessing quality of freshwater, estuarine, and marine sediments (Long et al., 1995; MacDonald et al., 2000; Sorensen et al., 2007). For examples, Ashtabula River in Ohio was found that concentrations of total PAHs and PCBs in sediment samples were likely high enough to have caused the reduces survival or length of amphipods, based on exceedances of mechanistically based SQGs (Ingersoll et al., 2009).

PBDEs are brominated flame retardants (BFRs) that were widely used in various applications including in furniture (polyurethane foam), wire and cable insulation, and electronics and computers (high impact polystyrene). Most commercial products principally contain penta-, octa- or deca-BDE mixtures. The annual global consumption of PBDEs in 1992 was about 40,000 tons, but by 2001 this had increased to approximately 67,000 tons (de Wit, 2002). BFRs are not produced in Taiwan but are imported from various countries (MOEA, 2011). From 1997 to 2003 more than 2500 tons of BFRs were imported and used per year in Taiwan (Fig. S1), with deca-BDE being one of the most used BFR (MOEA, 2011).

PBDEs and PCBs can disturb endocrine hormone homeostasis and affect the equilibrium of thyroid hormones (THs), some effects

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have been observed in rats, seals, fish and humans (de Wit, 2002). Prenatal exposure to PBDEs and PCBs has been found to be associated with reduced total thyroxine (TT4) and free T4 (FT4) in neonates (Herbstman et al., 2007). Several recent environmental studies have indicated increasing levels of several tetra- to deca-BDE isomers in marine mammals, sediments, bird eggs and human tissues (de Wit, 2002). Increasing concentrations of PBDEs in the environment have been attributed to several causes, including increased disposal of outdated electronic equipment and volatile losses from products still in use (Hale et al., 2002). Because of the widespread use of PBDEs as flame retardants, there is a growing need to determine their levels in various environmental compartments to enable assessment of the ecosystem impacts of these compounds.

The study area in Taiwan, which includes the Kaohsiung and the Tainan coasts, is heavily industrialized with steel manufacturing and petrochemical processing complexes, and encompasses the Southern Taiwan Science Park. The Kaohsiung coast also receives wastewater from three ocean outfalls (Zuoying, Jhongjhou and Dalinpu), two of which carry effluents from industrial parks involving petrochemical, steel, ship building and electrochemical industries (Yang, 1995). There is also significant input of industrial wastewaters to the Gaoping estuary from the Linyuan industrial park, via the Gaoping River and the Dalinpu ocean outfall pipe.

In the Asia-Pacific region most information on PBDE and PCB contamination comes from Japan and China (Mai et al., 2005; Ohta et al., 2002; Peng et al., 2009; Watanabe et al., 1995). Only one report of PBDEs in environmental samples from Taiwan has been published (Jhong and Ding, 2008), and this involved a limited number of samples and sampling locations. As a result, insufficient data on these chemicals are available to evaluate their distribution patterns, potential sources, effects and fate. The aim of this study is to determine levels of PBDEs and PCBs in sediments of southwestern Taiwan in order to assess the contamination status of the aquatic environment. Sampling sites were selected to determine the spatial distribution of PBDEs and PCBs in a coastal zone that has various levels of industrial and agricultural activity. A statistical analysis, including principal component analysis (PCA), of the data matrix was undertaken to investigate the relationships of regional signatures of PBDEs and PCBs to possible point sources.

2. Materials and methods

2.1. Sample collection

Surface sediments were collected at 57 stations in the coastal area of southwestern Taiwan using a Shipek grab sampler aboard the research vessel ORIII (cruises 1110, 1119 and 1120) between November and December 2005. Based on its location, each sampling station was assigned to one of the following groups: the Tainan coast (stations A1–A18), the Kaohsiung coast (off shore stations: B1–B6; near shore stations: C1–C23), the Gaoping estuary (stations D1–D8), the Zengwun River estuary (station E1) and the Agongdian River estuary (station E2) (Fig. 1). Following sediment collection, samples were placed at 4 °C in pre-combusted (450 °C for 4 h) amber glass bottles covered with solvent-rinsed aluminum foil, and transported to the laboratory. Sediment samples were wet-sieved (stainless steel sieve, 1000 μm mesh size) to remove gravel and detritus, and the resulting slurries were freeze dried, ground, and stored frozen (−20 °C) until extracted.

2.2. Materials and chemicals

All solvents used were of super solvent grade and were obtained from Merck Co. (Darmstadt, Germany). Florisil was pre-combusted (550 °C, 15 h) before use. Sodium sulfate was pre-cleaned and purified by heating at 450 °C, and stored in a sealed container. Individual PBDE and PCB compounds analyzed during the study are listed in Table S1. Internal standard solutions of a ^{13}C-labeled BDE-209 (2,2′,3,3′,4,4′,5,5′,6,6′-decabromodiphenyl ether, BDE-209L) and a ^{13}C-labeled CDE-86L (2,2′,3,4,5-pentachlordiphenyl ether, CDE-86L) were purchased from Cambridge Isotope Laboratories (Andover, MA). PCB calibration standards (Aroclors 1232, 1248 and 1262) and individual congeners of PCB-14, -30, -65, -166 and -204 were obtained from AccuStandard Inc. (New Haven, CT).

2.3. Extraction and analytical procedures

Dry sediments (20 g) were extracted with 150 mL dichloromethane (DCM) for 24 h using Soxhlet system. The extraction protocol was a modification of a method for PBDEs, described previously (Stapleton and Baker, 2003; Tuerk et al., 2005). The resulting organic phase was reduced to approximately 5 mL using a rotary evaporator (Buchi R-3000), and passed through a glass column packed with 8 g of 2.5% (w/v) deactivated florisil and baked anhydrous sodium sulfate (1 cm). The organic portion was eluted twice with 35 mL of petroleum ether. The first 35 mL of eluent was discarded, while the second 35 mL of eluent was collected and concentrated to approximately 5 mL by rotary evaporation. The volume of extract was further reduced to less than 1 mL under a gentle stream of nitrogen (99.99%; purified by passage through an activated carbon column), and analyzed using gas chromatography–mass spectrometry (GC−MS) and a gas chromatography–electron capture detector (GC–ECD).

Sample analysis was performed using a Varian CP-3800 gas chromatograph coupled with a Model 320 mass spectrometer using negative chemical ionization (NCI) in the selected ion monitoring (SIM) mode. A VF-5MS (10 m × 0.53 mm × 0.25 μm film thickness) rapid capillary column was used for the determination of PBDE congeners. The initial column oven temperature (80 °C; held for 0.5 min) was increased to 210 °C at 30 °C/min (held at 210 °C for 2 min), then increased to 310 °C at 25 °C/min (held at 310 °C for 3.17 min). Manual injection of sample (1 μL) was conducted in the split mode. The temperature of both the injector and detector was 300 °C.

The concentrations of PCB congeners were quantified using an Agilent 4890D gas chromatograph equipped with a ^{63}Ni electron capture detector and a 5% phenyl–methyl silicon capillary column (DB-5; 60 m × 0.25 mm × 0.25 μm film; J&W Scientific). Hydrogen and nitrogen were used as the carrier and make-up gases, respectively. The oven temperature program was: 100 °C for 2 min, 100–170 °C at 4 °C/min, 170–280 °C at 3 °C/min, and 280 °C for 5 min. The temperatures of the injector and detector were 250 and 285 °C, respectively. The identification and quantification of PCB congeners follows the method of Fang et al. (2008), in which the concentrations of PCB congeners were determined in the presence of a mixed Aroclor standard. For quantification, 35 ng of each of the PCB congeners PCB 30 and PCB 204 were added to each sample extract, as internal standards. Quantification of PBDEs and PCBs was carried out with the internal calibration procedure. The congeners in the sample extracts were determined on the basis of their chromatographic retention times relative to the internal standards.

2.4. Particle size and total organic carbon determinations

A portion of the sieved sediment slurry was analyzed for particle size distribution using a Coulter LS Particle Size Analyzer (Jiang et al., 2009). The total organic carbon (TOC) content of the sediment was determined using a CHNOS elemental analyzer (Vario EL III; Hanau, Germany), following removal of carbonates with HCl.