

DISTRUBUTION OF PBDES IN SURFACE SEDIMENTS FROM THE BERING SEA, CHUKCHI SEA AND CHUKCHI PLATEAU

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Abstract

11 PBDEs congeners were analyzed for 24 surface sediment samples, which were collected from the Bering Sea, Chukchi Sea and Chukchi Plateau during the 3rd Chinese National Arctic Research Expedition in July-September, 2008 and 8 congeners were detected. Concentrations of Σ PBDEs (sum of PBDE congeners without BDE209) and BDE-209 varied from 3.58 to 148.95 pg/g and from n.d. to 804.91 pg/g, respectively. The spatial variability of PBDEs concentrations indicated that BDE-209 was the predominant congener detected in most stations, consistent with the fact that technical deca-BDE mixtures are presently the dominant technical PBDE mixtures. Slightly different PBDE compositions were observed among samples collected from stations near the Barrow Point, indicating that technical penta-BDE mixture may be an important source from Alaska.

Introduction

Polybrominated diphenyl ethers (PBDEs) have been widely used as flame retardants to reduce or inhibit the risk of fire in a variety of plastics, paint, furniture and textile and so on [1, 2]. These compounds have been found widespread in different media (i.e. sediment, soil, water, air, various organisms and human tissues) [3, 4]. They have caused great environment concern due to their persistence, widespread distribution via atmospheric transport, potential for bioaccumulation, toxic for ecosystem and long-range transport [4, 5]. Major commercial products principally contain penta-, octa-, and deca-BDE mixtures. The penta-product contains a mixture of tetra- to hexa-BDEs including BDE-47, BDE-99, BDE-100, BDE-153 and BDE-154, as well as trace amounts of BDE-17 and BDE-28. The octa-product consists primarily of BDE-183, followed by BDE-153 and BDE-154, whereas the deca-product is mostly composed of BDE-209 (>97%) [6, 7]. In May, 2009, tetra- and penta-BDE, hexa- and hepta- BDEs were included in the global Convention on POPs (Stockholm Convention).

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PBDEs have physical-chemical properties similar to those of PCBs [8]. Therefore, it is possible for these compounds to be transported to the Arctic by the same pathways as PCBs to the Arctic. Previous studies showed that PBDEs are widespread in the Arctic and that levels are increasing and that PBDEs will undergo long-range transport, deposition and revolatilization from use regions to the remote Arctic areas [9]. Therefore, the Arctic is an important region to evaluate PBDEs pollution. Sediments are widely used to study the source, pathway and sink of the contaminants due to their role in transport and storage [10]. However, studies on Arctic sediments are quite limited, including the High Arctic Canadian archipelago, the northern Norway and the Kola Bay [4]. The primary goal of this study was to examine the concentrations and spatial distribution of PBDE in surface sediments of the Bering Sea, Chukchi Sea and Chukchi Plateau. In addition, the potential sources were also discussed.

Materials and Methods

Sample Collection. A total of 24 surface sediment samples were collected from the Bering Sea, Chukchi Sea and Chukchi Plateau during July~ September, 2008 (Fig.1). Sediments were collected using a stainless steel grab sampler. The top 5-cm layer of sediments was scooped using a pre-cleaned stainless steel scoop into solvent-rinsed aluminum containers. All samples were stored at -20 °C until further analysis.

Materials. A standard mixture of PBDEs except for BDE-183 and BDE-209 and individual standards of BDE-183 and-209 were purchased from Accu Standards (New Haven, CT). A standard solution of PCB-209 was obtained from Ultra Scientific (North Kingstown, RI). Individual standard solutions of ¹³C-labeled-PCB-141 and PCB-208 were purchased from Cambridge Isotope Laboratories (Andover, MA). All solvents and reagents used were AR grade and all organic solvents were re-distilled using glass system. Neutral silica gel (80–100 mesh) and alumina (100–120 mesh) were Soxhlet extracted with a mixture of dichloromethane and n-hexane (1:1) for 72 h before used. Once drying under room temperature, silica gel was baked at 180 °C for 12 h. Sodium sulfate was baked at 450 °C and stored in sealed containers.

Pretreatment and Instrumental Analysis. The detailed treatment and instrument analysis conditions were described in the literature [1]. Brief description of these methods was as followed: homogenized samples(50g) were extracted with a mixture of acetone and hexane (1:1, V/V) for 48h after spiked with ¹³C-PCB-141 and desulphurized with activated copper. The extract was concentrated and exchanged to n-hexane and fractionated on a 10 mm i.d. silica/alumina column. The PBDE mixture was eluted with 80 ml of hexane: dichloromethane (1:1, V/V), and the final extract was reduced to 200 µl under a gentle N₂ stream. ¹³C-PCB-208 was added to all extracts as the internal standard before instrumental analysis. Instrumental analysis was performed with a Shimadzu Model 2010 gas chromatograph (GC) coupled with a Model QP2010 mass spectrometer (MS) using

negative chemical ionization (NCI) in the selected ion monitoring (SIM) mode. A DB-XLB (30 m×0.25 mm i.d., 0.25 μm film thickness) capillary column was used for the determination of PBDE congeners except for BDE-209 and a CP-Sil 13 CB (12.5m×0.25mm, i.d., 0.2 μm film thickness) capillary column was used for BDE-209.

Quality Assurance and Quality Control. For each batch of 8 field samples, a method blank (solvent), a spiked blank (11 PBDE congeners spiked into solvent), a spiked matrix sample (11 PBDE congeners spiked into pre-extracted sediment) and a sample duplicate were processed. Only small concentrations of BDE-47 and -99 were found in procedural blanks, and they were appropriately subtracted from those in the sample extracts. The surrogate recoveries for ¹³C-PCB-141 were 79.1±8.3%. The relative percent difference for individual PBDE congeners identified in paired duplicate samples (n=3) was all<20%. Recoveries of 11 PBDE congeners ranged from 87.4% to 114.8% with relative standard deviation (rsd) <11.5% in spiked blank and 83.1~103.6% with rsd.<10.5% in spiked matrix samples. Concentrations in this paper were not surrogate recovery corrected.

Organic Carbon Determination. Sediment organic carbon was determined with an elemental analyzer (CHNS Vario EL III, Elementar) after removal of carbonates with 1:3HCl.

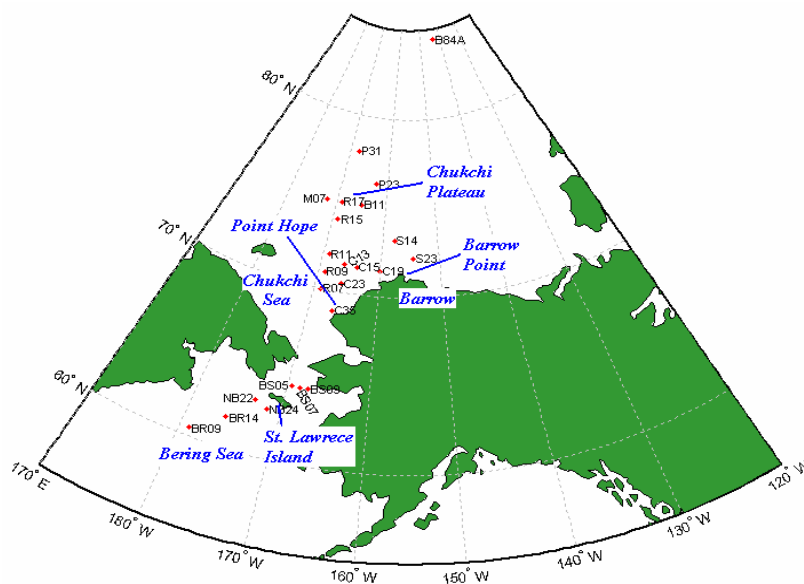


Fig.1 Map of Sampling Stations

Results and Discussion

Concentration and distribution. Eight PBDE congeners including BDE-47, 99, 100, 153, 154, 183, 138 and 209 were found in the samples, indicating that the contaminants were widespread in the study area. The concentrations of Σ PBDEs (in this paper, Σ PBDEs refers to the sum of PBDE congeners except for BDE-209) varied from 3.54 to 148.95 pg/g (dry weight) with a mean value of 34.86 pg/g and those of BDE-209 ranged from n.d. to 804.91 pg/g with an average of 108.78 pg/g. In general, the concentrations of BDE-209 were approximately 1~2 orders of magnitude higher than those of Σ PBDEs in the area around the St. Lawrence Island and the offshore area near the Point Hope. On the contrary, the concentrations of BDE-209 were lower than those of Σ PBDEs in the Chukchi Sea and Chukchi Plateau, including the stations near the Barrow Point.

The average concentrations of Σ PBDEs decreased in the order of Chukchi Plateau, Chukchi Sea and Bering Sea (including Bering Strait). It is obviously that samples collected from the north of the Barrow Point had substantially higher concentrations of Σ PBDEs than those in collected from other geographical sediments except the M07 station. This may be due to the potential source from northern Alaska. The relatively low concentrations of Σ PBDEs are located in the Bering Strait. The concentrations of the BDE-209 did not show apparent distribution trend in the study area while the extremely high value found in the southwest Bering Sea and the stations on the Point Hope coast. This is presumably due to the impact of point source inputs from the terrestrial.

Concentrations of PBDE in sediments have been reported for various regions in the world. However, concentrations in the Arctic sediments reported before are quite limited. They are located in remote sites in Canada, Russia and Norway and the concentration in these sites are quite familiar and higher than those in freshwater sediments except the Russian site of Polyarnny ^[4]. By comparison, most stations in our study had concentrations higher than 5.00 pg/g and 10 pg/g for Σ PBDEs and BDE-209, respectively. For Σ PBDEs, it is higher than those in the near shore sediments in the Arctic while it is lower for BDE-209.

PBDEs congener pattern and potential source. BDE-209 played a dominant role in the total PBDEs, especially in the area around the St. Lawrence Island and the offshore area near Point Hope with the contribution of BDE-209 ranged from 44.27% to 97.73% of the total PBDEs. This is probably due to the fact that commercial deca-BDE makes up most of the PBDEs use around the world ^[7]. However, in the Chukchi Plateau and the area near Barrow Point, BDE-209 contributed only 11.34~64.81%. This may be result from different formula of PBDEs used in different areas. BDE-99 is the predominant congener among the Σ PBDEs (with BDE-209 excluded), with an average relative abundance of 47.67%, followed by BDE-47, BDE-153 in the samples. BDE-99 and BDE-47 were the predominant compounds of the tetra- to hepta-BDEs in most staitons. The relative abundances of BDE-99 and -47 were generally greater than 50% of Σ PBDEs, similar to the composition of the penta-BDE mixtures ^[11]. These two congeners, couple with BDE153 and 154 comprised of 82~100% of

the Σ PBDEs, indicating that the technical penta-BDE mixture was also an important source. Further more, the ability of the particle-bound congeners BDE-47, -99, -153 to increase with the temperature decrease and the low concentrations of PBDEs seemed to suggest that atmospheric deposition was a significant input pathway^[6, 12, 13]. It may also suggest that different types of commercial penta-BDE formulations used in different regions, or PBDE congener fractionation occurring during their transport in the environment and partitioning in various environmental media due to their different physicochemical properties.

The correlations among the PBDE congeners samples were examined to infer their potential sources. The correlations are close among BDE-47, BDE-99 and BDE-154 ($R^2 > 0.68$) while the correlations between BDE-209 and other congeners are low ($R^2 < 0.05$). This indicated that most of the tri- to hepta-BDEs were not originated from degrade of deca-BDEs and that present-day commercial PBDE are the likely source of PBDEs to the area. Further more, the poor relations between the BDE-209 and the individual congeners may indicate that the mechanisms were different with which individual PBDEs were transported to the study area. The strong correlations between the BDE-209 and Σ PBDEs ($R^2 > 0.7$) proved the dominance of BDE-209 in sediments except the extremely high stations.

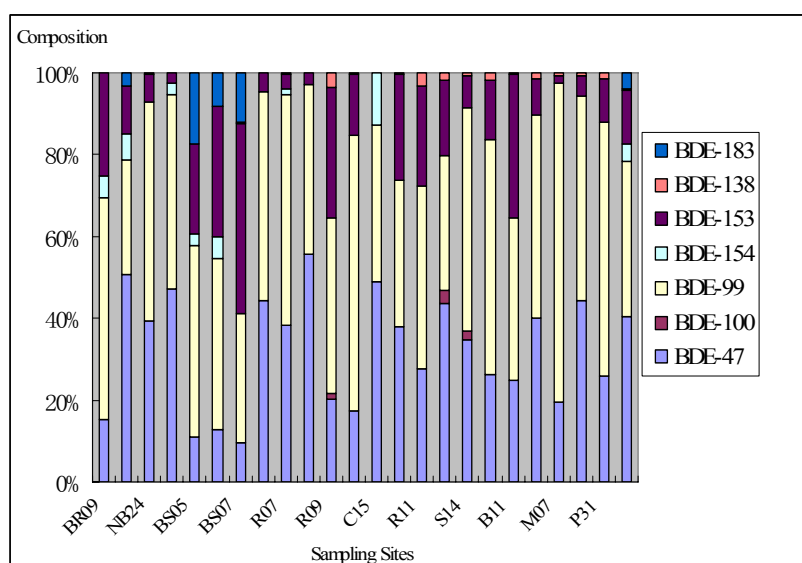


Fig.2 Percentage Contributions of 7 BDE congeners in surface sediments from the study area

Correlation of PBDEs with TOC and BC. PBDEs were expected to be well associated with organic carbon-rich particles due to their high hydrophobicities. Therefore, congener-specific partitioning among sediments of total organic content and black carbon content is expected, and may also explain the BDE distribution patterns. However, low correlations ($R^2 < 0.15$) of the BDE-209 and Σ PBDEs with TOC and BC

were found in our study. The poor relations may result from the effect of transport, mixing, deposition and input of PBDEs.

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