

ARE CURRENT CONCENTRATIONS OF PHAS IN LARGE RESERVOIR SEDIMENTS AT LEVELS OF CONCERN FOR THE HEALTH OF AQUATIC BIOTA

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Introduction

Polyhalogenated aromatic hydrocarbons (PHAHs) represent a large family of highly lipophilic and environmentally persistent substances, of which polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs) are two subfamilies that were of great concern in the present study, PBBs and PBDEs are applied to a wide range of commercial products like electronic circuitry, textiles, and plastics to improve fire resistance (WHO, 1994a; b). Polychlorinated biphenyls (PCBs) were the third and last subfamily considered in the present study. PCBs are industrial chemicals that have been used from the 1930s to 1974 in electrical capacitors and transformers, as lubricants, cooling fluids, and hydraulic fluids, and also in adhesives and plasticizers (WHO, 1993). Their occurrence in the environment is mainly the result of disposed products which contain them. Being highly resistant to degradation processes both brominated flame retardants (BFRs) and PCBs are persistent in the environment; furthermore, being lipophilic, they are expected to bioaccumulate readily and thereby present a potential ecological risk. Animal studies showed that the PHAHs in these three subfamilies not only were they capable of disrupting endocrine functions but could also induce neurodevelopmental, hepatic, reproductive, and other adverse health effects.

Sediment in water-supply reservoirs is an important environmental concern because sediment may act as a sink for water-quality constituents and as a source of constituents to the overlying water column and biota. PHAHs in sediment can pose potential health risks to aquatic biota. Therefore, sediment quality represents an important indicator for assessing water-quality and potential effects of PHAHs on aquatic biota.

Research on PHAHs in recent years mainly focused on highly polluted waters by Chinese researchers (Fu *et al.*, 2003), however, only few reports on PHAHs in natural waters are available and little is known about the current status polluted by PHAHs. Accordingly, an exploratory effort was made in the present study to monitor the sediment levels of 55 PHAHs in samples collected from six selected large reservoirs. The study sought to answer two questions: (1) how is the current contamination status of PHAHs in sediment from these large reservoirs; (2) are they at levels of concern for the health of aquatic biota?

The reservoirs were considered in the present study including Dht, Yc, Wk, Xdy, Sx, and Djk, which are all water-supply reservoirs. Their water-storage capacity was greater than 0.3 billion cubic meters. The former four reservoirs located Hebei Province, Sx and Djk located Hubei Province, China. The sediment samples were collected from fixed cross-sections for routine monitoring in these reservoirs.

This exploration represented the first of its kind in reporting extensively the recent levels of PBBs, PBDEs, and PCBs in sediments from the six large reservoirs in China. Information obtained from this type of exploration may also be very useful for subsequent assessment of drinking-water safety and the aquatic ecological risk at issue.

Materials and Methods

56 surface sediment samples (each weighing ~ 0.1 kg, at the top 0-10 cm layer) were collected from 2007 to 2008 in the selected water-supply reservoirs. Each sample was placed into a separate chemically-clean glass bottle, and labeled with a unique code and the proper sampling date. All samples were transported to the analytical laboratory as soon as possible and continued to be stored in the dark at 4°C until analysis.

The following standards were obtained from the Cambridge Isotope Laboratory (USA): 21 PBB congeners; 7 PBDE congeners; 27 PCB congeners; and surrogate standards pentachloro-nitrobenzene (PCNB), 2,4,5,6-tetrachloro-m-xylene (TMX), and PCB209. All solvents used (hexane, acetone, and methylene chloride) were of pesticide grade (Promochem, Germany). Silica gel (100-200 mesh) was also purchased from Promochem.

The sediment samples were all freeze-dried. The dried sediment were directly ground into powder in a mortar and then sieved to pass a 100 mesh for subsequent analyses. About 10 g of these residues from each sample, mixed with activated copper powder and diatomite, was introduced into a pre-cleaned stainless steel cells (100 mL volumes), and extracted by an ASE 300 instrument (Dionex, CA, USA) using an n-hexane/methylene chloride (1:1, v/v) solution. For this preparation process, TMX, PCNB, and PCB209 were added to each sample as surrogate congener standards. The extract from each sample was then concentrated to about 1 mL by rotary evaporation. The concentrated extracts were further cleaned individually by a multilayer silica gel column containing: 2 g of anhydrous sodium sulfate; 8 g of silver nitrate (AgNO₃) silica (10% AgNO₃ w/w); 2 g of deactivated silica (3.3% organic-free reagent water w/w); 15 g of acidic silica (44% conc. sulphuric acid w/w); 1 g of deactivated silica (3.3% organic-free reagent water w/w); and 2 g of anhydrous sodium sulfate. The first fraction eluted with n-hexane (100 mL) was used to concentrate the PCB congeners, with the second fraction (eluted with 10% methylene chloride in 80 mL n-hexane) intended for collection of the PBB and PBDE congeners. The eluants were concentrated separately to about 1 mL, again by rotary evaporation. The solvent of each sample was concentrated by gentle nitrogen stream at 25°C and redissolved in 200 µL n-Nonane.

The chemical analysis was performed using a Varian CP3800/300 triple-quadrupole system in combination with a capillary VF-5-MS (5% phenyl/95% methyl silicone, 30 m, 0.25 mm i.d., 0.25 µm film thickness, Varian, USA). The column oven temperature was programmed from 90°C (initial time, 1 min) to 250°C at a rate of 4°C min⁻¹, then from 250°C to 300°C at a rate of 25°C min⁻¹, and held for 5 min. The GC injector temperature was maintained at 260°C, with the temperatures of the MS ion source and of the transfer line being kept at 200°C and 250°C, respectively. The carrier gas was helium at a constant flow rate of 1.5 mL min⁻¹, the collision gas was Argon. The mass spectrometer was operated in the electron impact (EI) ionization mode for analysis PCBs. The MS/MS conditions in the multiple reaction monitoring (MRM) mode are optimized. Samples (1 µL) were injected in the splitless mode with a solvent delay set at 6 min. The mass spectrometer was operated in the electron capture

negative ionization (ECNI) mode for analysis PBBs and PBDEs. Helium and methane was used as carrier gas and reaction gas, respectively. The multiplier voltage was set to 1200V.

Results and Discussion

PBBs in sediment

Both of Geometric Means Σ PBBs in the reservoir sediment samples from the two provinces are 0.4 ng g⁻¹ dw (Table 1), PBB1, 4, 10, 30, 31, 53, 103, and 155 were the most abundant PBB congeners in the samples from Hubei Province. PBB1, 3, 4, 10, 31, 53, and 103 were the most abundant PBB congeners in the samples from Hebei Province. Low-brominated PBBs (including 1, 3, 4, 10, 30, 31, and 53) were seen to have accounted for >57% of the total PBBs observed in sediments.

In the earlier study, Zhao *et al* (2008) made a similar observation finding that the low-brominated PBBs were the principal congeners in the e-waste residues and surface soil. High-brominated PBBs may metabolize to their lower-brominated congeners through exposure to light (e.g., UV radiation, direct sunlight) and through biological activity in the environment (WHO, 1994a). In addition, dry gaseous deposition from the atmosphere might be a source of low-brominated PBBs in sediments. Results from other studies are consistent with the assertion that low-brominated PBBs were the predominant congeners observed in sediments. Vetter *et al* (2008) found that PBB103 and PBB155 can be obtained by debromination of higher-brominated biphenyls, and PBB103 and 155 were the predominant PBB congeners in the bird egg samples. Their findings support the observation that the dominant levels of 103 and 155 observed in the sediment samples in this study. The congener PBB153 was the principal component in commercial hexabromobiphenyl, which accounted for 60-80% of the total weight (WHO, 1994a). However, only trace PBB153 was detected in < 5% of samples in this study. This unexpected finding suggested that PBBs found in sediments could source from other technical PBBs mixtures other than hexabromobiphenyl. More in-depth investigations are needed for determining the possible sources of sediment contamination with PBBs.

PBDEs in sediment

As shown in Table 1, there was a comparable PBDEs level between these sediment samples from Hubei (G.M. = 0.26 ng g⁻¹ dw, n = 36) and Hebei Province (G.M. = 0.38 ng g⁻¹ dw, n = 20). PBDE28, 47, and 99 were the predominant PBDE congeners, accounting for > 89% of the total PBDEs in sediments.

Among the three main commercial PBDE mixtures pentaBDE, OctaBDE, and DecaBDE, only pentaBDE mixture contained 0-1% of triBDE (i.e., PBDE 28/33). Whereas PBDE28 was found to be the most predominant PBDE congener in these sediments, this finding suggested that there might be new inputs of this isomer. Atmospheric deposition which contains highly transportable congeners could be plausible source of these low-brominated PBDEs in sediments (Jiao *et al.*, 2009). In addition, Li *et al.* (2008) proved that PBDE28 was the predominant photoproducts of PBDE47 in surfactant micelles, the degradation of high brominated congeners to lower brominated ones could also contribute to the high proportion of PBDE28 in sediments observed. PBDE47 and 99 was reported to be the main isomers in commercial pentaBDE product, which accounted for 28% and 43% of the commercial pentaBDE Product (DE-71b), respectively. Many researchers also found that PBDE47 and 99 are the most predominant congeners in the lake sediment samples (Watanabe and Sahai, 2003), these facts

supported well the above-mentioned finding in this study.

PCBs in sediment

Among the three PHAH subfamilies, the measured level shows that PCBs had the highest concentrations in the reservoir sediment samples, with Geometric Means 8.48 ng g⁻¹ dw from Hebei Province and 6.67 ng g⁻¹ dw from Hubei Province. PCB18, 28, 52, and 8 were the most predominant PCB congeners in sediments from Hebei Province. PCB138, 153, 28, and 52 were the most predominant PCB congeners in sediments from Hubei Province.

There are two main commercial products made in China including Trichlorobiphenyl (9000 ton) and Pentachlorobiphenyl mixture (1000 ton) from 1965 to 1974. Trichlorobiphenyl mixture contained 42% chlorine, which was similar to Aroclor1242, used widely as transformer and capacitor oils, while Pentachlorobiphenyl mixture contained 53% chlorine, similar to Aroclor 1254, used mainly as paint additive. PCB8, 18, 28, and 52 were the major PCB congeners in Trichlorobiphenyl mixture, accounting for 7.05%, 8.53%, 8.5%, and 3.53% of the total weight, respectively. Therefore, transformer and capacitor oil containing Trichlorobiphenyl mixture is the possible source for low-chlorinated biphenyls (i.e., PCB8, 18, 28, and 52) observed in sediments from Hebei Province. Ren *et al* (2007) also observed a similar finding that tri-PCB (55%), followed by di-PCB (31%) are the major PCB homologues in Chinese background soils. PCB138, 153, and 52 were the major PCB congeners in Pentachlorobiphenyl mixture, which accounted for 5.8%, 3.7%, and 5.4% of the total weight, and Pentachlorobiphenyl mixture used widely as paint additive. Such facts lend further support of the notion that source of PCBs in local reservoirs environment in Hubei Province are possibly attributed to leaching from these products containing Pentachlorobiphenyl mixture.

Potential risk to aquatic biota

Sediment quality guidelines were used to evaluate the sediment quality and potential risk to the aquatic biota in the selected reservoirs. Level-of-concern concentration adopted by USEPA are referred to as the threshold-effects level (TEL, 34.1 ng g⁻¹ dw for PCBs). None of the PCBs observed values in the samples (ranging from 2.45 to 22.44 ng g⁻¹ dw) exceeds the freshwater sediment TEL (34.1 ng g⁻¹ dw), which shows toxic biological effects on aquatic biota (such as benthic organisms) are negligible due to PCBs contamination in these sediments.

At present, there are still no sediment quality guidelines for PBBs and PBDEs, the observed values of PBBs and PBDEs were thus compared with those results reported recently in the literature. The levels of PBBs and PBDEs in these reservoirs sediments (Σ PBBs 0.40 and 0.42 ng g⁻¹ dw; Σ PBDEs 0.26 and 0.38 ng g⁻¹ dw) were found comparable to those in relatively uncontaminated freshwater areas. For example, PBBs ranges from 0.02 to 0.33ng g⁻¹ dw; PBDEs ranges from 0.17 to 2.60 ng g⁻¹ dw in midlatitude and Arctic lake sediments. Thus, as far as the PHAHs under study are concerned, the sediments are relatively “clean” from the selected reservoirs.

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Table 1. Levels of PHAHs (in ng g⁻¹dw) measured in sediments collected from six large reservoirs located Hebei and Hubei Province, China^a

Pollutants	Sediments from Hebei Province (n = 20)			Sediments from Hubei Province (n = 36)		
	G.M.	Median	Range	G.M.	Median	Range
ΣPBBs	0.40	0.34	0.20-1.68	0.42	0.43	0.13-1.38
ΣPBDEs	0.38	0.38	0.08-0.87	0.26	0.28	0.08-0.47
ΣPCBs	8.48	8.66	2.45-22.44	6.67	6.46	4.17-12.11

^a PBBs: polybrominated biphenyls; PBDEs: polybrominated diphenyl ethers; PCBs: polychlorinated biphenyls; G.M.: geometric mean