Bull Environ Contam Toxicol (2010) 84:322–325
DOI 10.1007/s00128-009-9930-2

Polybrominated Diphenyl Ethers (PBDEs) Concentration in Sediments Located in the Vicinity of Fish Plant Effluent Outfalls in the Maritimes

Benoit A. Lalonde · William Ernst

Received: 10 September 2009 / Accepted: 18 December 2009 / Published online: 30 December 2009

Abstract Since polybrominated biphenyl ethers (PBDEs) are known to be present in various species of fish, it is likely that fish processing effluent would contain significant amount of PBDEs. The purpose of this study was to determine the PBDE concentrations in sediments located near fish plant effluent outfalls. The range of concentrations of PBDEs in marine sediments in Canada published in the literature was very similar to the results obtained in this study (0.015–5.12 ng/g, dry weight). The concentrations measured in this study for all three technical mixtures (2.78×10^{-3}, 1.92×10^{-3} and 2.02×10^{-3} mg/kg, respectively) were all below known toxicity thresholds (0.031, 9.1 and 76 mg/kg, respectively).

Keywords PBDEs · Fish plant · Sediment · Effluent

The seafood processing industry is of national economic importance in Canada with the highest numbers of facilities located in the Atlantic Provinces (Lalonde et al. 2007). The locations of seafood processing plants are scattered throughout the Atlantic Provinces since they were often built in proximity to the fishing grounds. Therefore, the majority of seafood processing plants are located in rural areas with little industrialization (Lalonde et al. 2007) and as such, the receiving environments are usually relatively unimpacted by typical urban-based anthropogenic pollution sources such as large sewage outfalls and, industrial outputs.

B. A. Lalonde (✉) · W. Ernst
Environment Canada, Water Science and Technology Directorate, 45 Alderney Dr, Dartmouth, NS B2Y 2N6, Canada
e-mail: benoit.lalonde@ec.gc.ca

Polybrominated dyphenyl ethers (PBDEs) have been used extensively worldwide as flame retardants, however, in the last few years, some jurisdictions have called for the control of the manufacture and emissions of PBDEs. Brominated dyphenyl ethers have congeners which range from bi to deca-brominated BDEs with the tetra to hexa-brominated congeners demonstrating properties most likely to result in bioaccumulation in organisms (Environment Canada 2006). PBDEs have been measured in a variety of environmental media such as air, soil, water (marine and freshwater), fish, mammals, birds, eggs, invertebrates, human blood, human breast milk and sewage sludge (Law et al. 2008). The concentrations in various matrices are often closely associated with organic content since these chemicals are hydrophobic (Environment Canada 2006). Effluents from fish processing plants have been shown to contain moderate quantities of organic substances (Lalonde et al. 2007) and therefore it is likely that sediment in the vicinity of the outfalls could be contaminated by PBDEs, however, no studies of PBDE concentration in sediment in the vicinity of fish plant processing have been published to date. The purpose of this study was to determine the PBDE concentrations of the sediments located in the receiving environment of fish plant effluent outfalls.

Materials and Methods

Sediment samples (250 mL) were collected in the receiving environment in proximity of five seafood processing plants in March 2006. The samples were collected by scuba divers along the prevailing current direction at; 0, 10 and 100 m from the plant outfall. While these plants may process more than one species in a year, the main species processed for each plant sampled were; lobster in Cap Pelé

and Ste Anne, shrimp in Lamèque, herring roe in Caraquet and crab in Tracadie.

The sediment samples were thoroughly homogenized and subsampled for analysis of sulphide, redox potential (Eh), and ammonia by specific ion electrodes. A subsample of each of the sediments were placed in tarred vessels and dried at 100°C for 24 h, those weights were used to convert results to a dry weight basis. The PBDE analysis was performed at AXYS (Sidney, BC) in accordance with EPA's Draft Method 1614 (EPA 2003).

Results and Discussion

This survey adds to the very limited data set of the concentration of PBDEs in marine sediment in Canada. Sather et al. (2006) reported PBDEs in marine sediments near fish farms ranged from 0.48 to 4.36 ng/g which is very similar to the results obtained in this study (total PBDEs from 0.015 to 5.12 ng/g, dry weight; Fig. 1). Total PBDE concentrations near Canadian pulp mills and urban areas ranged from 0.22 to 2.495 ng/g (Ikonomou et al. 2006) which again were similar to the concentrations in reported here; however, Ikonomou et al. (2006) did not measure the level of deca-BDE which accounted for most of the total PBDE in our samples. Measurements by Moon et al. (2002) and Nylund et al. (1992) in relatively unimpacted areas of Korea and the Baltic Sea showed similar concentrations of PBDEs in marine sediment (0.009–3.27 ng/g) as those from our study. However, the study by Van Zeijl (1997) found significantly higher total concentrations of PBDEs (up to 1,712 ng/g) in marine areas known to be impacted by industrialization.

In this study, the PBDE concentrations ranged widely as a function of location. Two stations had substantially higher concentration of PBDEs than all other stations; Ste Anne (100 m) and Tracadie outfall (0 m; Fig. 1). The

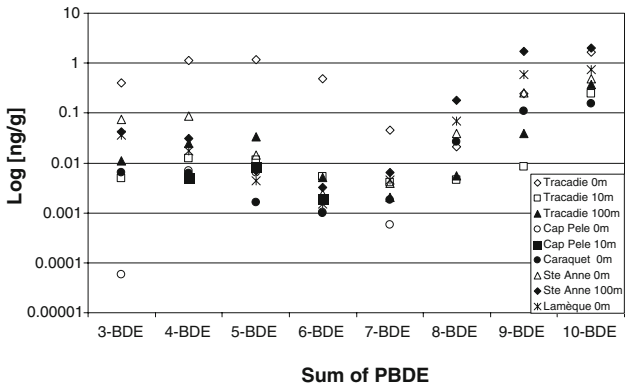

Fig. 1 Log transformed PBDE concentrations as a function of congeners of PBDEs at various locations and distances from fish plant effluent outfalls

sediment sample from the Ste Anne (100 m) station had the highest concentrations of PBDEs, sulphide and ammonia and lowest readings of redox in comparison to the samples obtained at the outfall and at 10 m distance from the outfall. It is possible that the breakwater located near the sampling station of 100 m could be acting as a barrier to suspended solids from the effluent outfall creating a depositional area for organic sediments and absorbed PBDEs. It is also possible there was an unknown effluent discharge in this area such as sewer (or grey) water from the fish plant or from adjacent homes or buildings since sewer waters have been shown to be a contributor of PBDEs in the environment (Environment Canada 2006; Sellstrom et al. 1998).

The high elevated concentration of PBDEs at the outfall in Tracadie indicates that the plant is the probable source of PBDEs in sediment. Also of interest is that the Tracadie 0 m sample contained the highest concentrations total PBDEs and also of tetra to hexa-BDEs congeners which have been shown to be bioaccumulative (Environment Canada 2006). The elevation of the bioaccumulative congeners could be attributed the specific species (snow crab) processed at the plant in Tracadie since Hale et al. (2001) reported that fish species have different metabolic potentials for PBDE congeners and have reported differences in congener ratios for various fish species. Crab also have increased exposure to sediments, compared with other species and PBDEs are also likely to partition to sediment (Environment Canada 2006). It is noteworthy that the species processed (snow crab, Northern shrimp, American lobster and Atlantic herring) at the fish plants where sampling occurred were not top predatory species which would tend to have higher concentrations of the tetra to hexa brominated congeners since these congeners have been shown to be bioaccumulative (Environment Canada 2006).

The ratios of the different type of congeners as a percentage of the sum of total PBDEs is informative since it helps to predict the bioaccumulation impacts of the concentrations of PBDEs selected in the sediment and it also facilitates speculation on the source of the PBDEs detected. With the exception of the Tracadie samples, all of the samples had the same congener distribution patterns (Fig. 1). The highest concentration of tetra to hexa-BDE (2.77 ηg/g) was measured in the sample collected at the outfall from Tracadie (Tracadie 0 m). The major contributor to the total PBDEs concentration was from the deca-BDE fraction of the samples with a range from 32% to 83% with four of the samples having 50% of the total PBDEs in the form of deca-BDE.

Similar ratios were shown in the Sather et al. (2006) study of marine sediments around fish farms in New Brunswick where deca-BDE made up from 42% to 84% of the total concentration of PBDEs. Similar ratios were also

reported in freshwater sediment by Li et al. (2006) which reported that BDE209 is clearly the dominant congener of the sediments of the great Lakes and this is in contrasts with low concentration of deca-BDE in humans and wildlife. Deca-BDEs were also the dominant congeners in the studies by Sellstrom et al. (1998) and Shen et al. (2006). Shen et al. (2006) reported that decaBDE in sediment reflect that environmental release were from the use of the technical mixture deca-BDE. Sather et al. (2006) also suggested that an elevated sediment concentration of deca-BDEs in sediment was because they are used widely. Environment Canada (2006) reported that 83% of worldwide production of PBDEs is deca-BDE.

The ratio of tetra to hexaBDEs to the total sum of PBDEs at the Tracadie (0 m) site ranges from nine to almost 100% of the total concentration of PBDEs. Both samples collected in Cap Pelé are mostly composed of tetra to hexa-BDEs. However, the concentration of tetra to hexa-BDEs in the samples in Cap Pelé is of the same order of magnitude as all other samples in this study. The main differences between the two samples from Cap Pele and all of the other samples are the lack of octa to deca-BDEs in these two samples. The lack of octa to deca-BDEs is probably not due to the transformation of these congeners to less brominated (tetra to hexa-BDEs) congeners since the tetra to hexa-BDEs in all samples in Cap Pelé are of similar concentrations than to those of all other sampling stations of this study. The lack of transformation of PBDEs in sediment is also discussed by Hale et al. (2006) which indicated that in general, PBDE congeners in sediment are known to degrade minimally. Sellstrom et al. (1998) suggested that the superlipophilicity (log $K_{ow} = 9.97$) of deca-BDE causes its high partitioning to sediment. Rayne et al. (2003) also suggested that the lack of octa to deca-BDEs in sediments was based on equilibrium partitioning theory in which heavier PBDE congeners have higher affinity to smaller sediment fraction (silt, clays colloidal and particulate organic carbon, organic detritus) since they have higher organic content and surface area. The sediment collected in the Cap Pelé location had the lowest proportion, of all samples, of clays and silt in comparison to the sand fraction which would explain the lack of detection of the heavier PBDE congeners as per the findings of Rayne et al. (2003).

Simple regressions between total PBDE concentrations and physical and chemical parameters yielded three statistically significant relationships; ammonia, sulphide and redox potential. It is important to note that all three parameters were significantly auto-correlated, however, the model using the sulphide concentration explained most of the variability of the PBDEs concentration of the dataset with an R^2 value of 88% ($p < 0.001$). However, it seems that the sulphide concentration in sediment is a better predictor of PBDE in sediment when compared to other published studies. In Rayne et al. (2003), PBDE concentration was predicted with the ratio of organic carbon to organic nitrogen content. The model by Rayne et al. (2003) explained 62% of the variability of the dataset. Rayne et al. (2003) explained that their predictive model points to wastewater input as source of PBDE in sediment. Another study detected organic matter content of the sediment as a predictor of PBDE in sediment (Li et al. 2006). The study by Li et al. (2006) found that organic matter content was significant, accounting between 63% and 73% of the concentration of total (less deca) BDE and 209-BDE, respectively.

The three risk quotients were calculated for the technical mixture of the congeners of PBDEs produced worldwide; one for penta-BDE (tetra to hexa-BDEs), one for hepta to nona-BDEs and one for deca-BDEs. Three risk quotients were calculated using an estimated no-effects value for benthic organisms (Environment Canada 2006) and the highest PBDE congeners detected in this study. Of all the samples collected in this study, the highest concentrations of PDBE congeners for penta-BDE, hepta to nona-BDE and deca-BDE were 2.78×10^{-3}, 1.92×10^{-3} and 2.02×10^{-3} mg/kg, respectively. The relatively lower estimated no-effects value for benthic organisms for penta-BDEs, hepta to nona-BDE and deca-BDE were 0.031, 9.1 and 76 mg/kg, respectively (Environment Canada 2006). All three risk quotients calculated were well below one which indicates minimal potential risk to benthic organisms from PBDE exposure in sediments collected in the vicinity of fish processing plants in the Maritime region.

Acknowledgments We thank Bertin Gauvin from La coallition pour la viabilité de l'environnement de Shippagan et des Îles Lamèque et Miscou, Simon Courtenay from Fisheries and Oceans Canada at the Canadian Rivers Institute and Monica Boudreau from Fisheries and Oceans Canada for their technical assistance in obtaining and analysing the sediment samples. We are also grateful to Paula Jackman and Ken Doe from Environment Canada's Environmental Quality Laboratory in Moncton (NB) for the ammonia, redox and sulphide results.

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