Bull Environ Contam Toxicol (2010) 85:170–173
DOI 10.1007/s00128-010-0086-x

Polybrominated Diphenyl Ethers Concentrations in Fish Processing Plant Effluent

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Received: 11 January 2010 / Accepted: 9 July 2010 / Published online: 21 July 2010

Abstract The total concentration of PBDEs in the wastewater from fish plants ranged from 82 to 35,055 pg/L which was higher than ambient concentrations measured in surface water samples in North America (6–158 pg/L). Based on the concentration of PDBES in the effluent, calculated daily discharge of PBDEs into the environment ranged from 0.03 to 13.34 g per day. The concentrations of PBDEs in the solid fraction of the effluent from this study has been calculated to range from 0.78 ng/g for scallop, to 3,505 ng/g for cod with herring having the second highest concentration of 1,534 ng/g.

Keywords PBDEs · Fish plant · Effluent · PBDE ratios

Polybrominated diphenyl ethers (PBDEs) have been measured in a variety of biological and environmental media. However, there are no known studies of PBDE concentration in effluent from seafood processing. It was hypothesized that PBDEs would be prevalent in effluent from fish processing since PBDES have been found previously in the tissue of fish and invertebrates (Law et al. 2008). The purpose of this study was to determine the PBDE concentrations in the effluent from fish processing plants located in Atlantic Canada.

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Materials and Methods

Effluents form eight plants, located in Atlantic Canada, processing, herring, cod, shrimp, lobster, Jonah crab, redfish, scallop and fish meal (herring) were sampled as part of this study. Final effluent samples from the seafood processing plants were collected with Sigmamotor 900 samplers. Composite samples were collected over the daily plant production period (up to 24 h). The samplers were set-up with Teflon tubing and a hexane rinsed 20 L glass carboy (surrounded by ice packs). A sample of at least 10 L was obtained at each processing facility. Once the sampling was complete, the carboy was stirred, its liquid content transferred into two 1 L amber glass bottles and kept cool with ice packs until overnight delivery to the laboratory. Sample were analysed for PBDEs at AXYS (Sidney, BC) in accordance with EPA's draft method 1614 (EPA 2003). Samples were also analysed for a variety of physical and chemical parameters in a study described in Lalonde et al. (2007).

Results and Discussion

The results of the analysis on the total sum of PBDEs as well as the tri to deca-BDEs congeners in fish processing wastewater are presented in Fig. 1. The PBDEs concentrations in fish plant effluent ranged from 82 to 35,055 pg/L which is above concentrations of PBDEs in surface water measured in previous studies from North America (6–158 pg/L) (Environment Canada 2006). However, concentrations of PBDEs in water samples are usually low since PBDEs have low water solubility and are usually associated with lipids (Environment Canada 2006). Therefore, it is not surprising that PBDEs concentrations

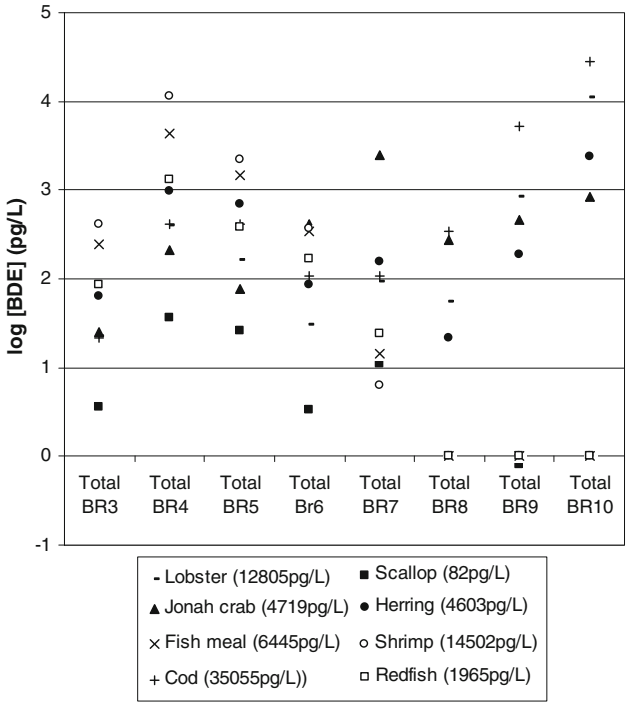

Fig. 1 PBDE concentrations as a function of brominated substituted groups for eight different effluents from seafood processors. Total PBDE concentrations in effluent are posted in the legend

detected in wastewater from fish processing plants in this study were one to three orders of magnitude higher than concentrations detected in surface water in North America. Calculated sums of PBDEs discharged to the environment have been calculated using the water usage of the fish processing plants and ranged from 0.03 g/day for scallop processing to 13.34 g/day for shrimp processing. Polybrominated diphenyl ethers have not been measured previously in fish processing wastewater and therefore direct comparison to our results is impossible. Polybrominated diphenyl ethers have previously been measured in samples from sewage treatment plants (STP) and in areas where various industrial complexes are located (Law et al. 2008). Most of the environmental samples associated with the studies above have focussed on the sewage sludge and sediment in the vicinity of the plants since PBDEs are hydrophobic are likely to be detected in sediments and not in the wastewater from industrial outfalls. However, a few studies have measured PBDEs in wastewater from STPs. Anderson and MacRae (2006) detected PBDEs concentrations in effluent from a sewage treatment plant in Maine with results ranging from 3.1 to 9 $\times$ 10^5 pg/L which is two to five orders of magnitude higher than our results (82–35,055 pg/L). North (2004) detected PBDE concentrations ranging from 4 to 29,000 pg/L in wastewater effluent from municipal treatment plant in California which is within the same order of magnitude as that from our study.

The PBDE ratios detected in environmental samples can also yield the chemical mixtures that are present in the environment since there are three main mixtures discharged to the environment. The three main mixtures are; penta-BDE, octa-DBE and deca-BDE (Environment Canada 2006). Penta-BDEs is a mixture of mainly tri to hexa-BDEs congeners, octa-BDE is a mixture of mainly hexa to octa congeners while deca-BDE is mostly made up of deca-BDE (Environment Canada 2006). Although uncertainty regarding the possible transformation products of decaBDE exists, there is sufficient evidence to conclude that some level of decaBDE phototransformation likely occurs in the environment and that lower brominated PBDEs are being formed during this process (Environment Canada 2006). This is of particular importance since it has been shown that the tetra to hexa congeners are highly bioaccumulative (Environment Canada 2006). Our study measured the concentrations of the individual congeners of tri-BDE to deca-BDEs which makes up the total concentration of PBDEs in wastewater (Fig. 1). Wastewater from the fish meal (herring), shrimp and redfish had no detectable concentrations of the octa to deca-BDE congeners once all results were blank corrected (Fig. 1). However, these three samples had some of the highest concentrations of the tetra to hexa-BDEs congeners with over 90% of their total PBDES in the tetra to hexa fraction (Fig. 1). Possible explanations for this results is the lack of exposure to the octa and deca-BDE mixtures or the debromination of the higher brominated congeners to the tetra to hexa fraction (Environment Canada 2006). The lowest proportion of the tetra to hexa congeners was measured for the lobster and cod samples with less than 5% of the total PBDE concentrations allocated to the tetra to hexa congeners. Both lobster and cod are bottom dwellers compared to the other species in this study and this may be affecting the type of congeners they accumulate. There might also be a lack of phototransformation of deca-BDE to tetra to hexa congeners within these species habitat which would explain the lack of tetra to hexa congeners in the cod and lobster effluent. The concentration of tetra-BDE for the shrimp processing wastewater was the highest of all samples and exceeded the total sum of tetra to hexa-BDEs of all other samples in our study (Fig. 1). The wastewater from the plant processing shrimp had the highest total organic carbon concentration of all samples which may, in part, explain the high concentration of tetra-BDE in the sample since PBDEs have been shown to have a high affinity to particles (Sellstrom et al. 1998). A possible explanation to the high concentrations of tetra to hexa BDE in certain samples is due to the highly bioaccumulative nature of the tetra to hexa congeners (Environment Canada 2006). The other potential source for PBDEs (especially Hepta-, Octa-, and Deca- BDEs) in the wastewater samples from seafood

processing plants would be from polymer mouldings, panels, synthetic rubbers and moulded plastics which come into contact with the fish during the transport, warehousing and processing phases.

To compare the concentrations of PBDEs in wastewater with levels in biota, the wastewater data has to be transformed into a solid fraction (i.e., ng/g). Since it is expected that PBDEs entering the environment will tend to bind to the organic fraction of particulate matter (Environment Canada 2006) and if we assume that the PBDEs source in seafood processing wastewater is only from the organism processed (and not from any plastics used in the processing), the levels of volatile suspended solids (VSS) or total organic carbon (TOC) in the effluent can be used as a surrogate for the organic fraction of the sample. Therefore, the sum of PBDEs (as a solid fraction) can be calculated by dividing the aqueous concentration (pg/L) of the PBDEs by the amount of VSS or TOC in a 1 L sample (mg/L). Although the concentrations of PBDEs calculated using VSS and TOC show similar trends with regards to the levels found in the different sources. The concentrations of PBDEs in the solid fraction of the effluent from this study has been calculated to range from 0.78 ng/g for scallop, to 3,505 ng/g for cod with herring having the second highest concentration of 1,534 ng/g. A combination of high lipid content in cod and herring as well as life characteristics (feeding habits, habitat) of these two fish species are believed to be linked to the higher concentration of PBDEs in these species. A similar range of PBDEs (0.726–1,250 ng/g) in fish tissues from North America was measured in studies by Rayne et al. (2003) and Johnson and Olson (2001).

The solid fraction of tetra to hexa-BDE were calculated for all wastewater samples. Tetra- to hexa- BDEs were used as they have the highest potential to bioaccumulate (Environment Canada 2006). Redfish and herring had the highest solid fraction concentrations of tetra to hexa BDEs and overall the concentrations ranged from to 1.86 to 587 ng/g for all samples analysed. In comparison, a study by Brown et al. (2006) of BDE-47, 99, 100, 153 and 154 (tetra to hexa-BDEs) showed total BDE ranging from 13 to 1,023 ng/g lipid of various fish species from the coast of California. The levels of PBDEs in the study by Brown et al. (2006). are of similar levels to those of this study although our PBDE concentrations were based on the organic fraction of wastewater instead of the muscles used in the Brown et al. (2006) study to determine PBDE concentrations.

Simple regression between PBDE versus ten different physico-chemical parameters measured in the water samples (Lalonde et al. 2007) yielded two statistically significant relationships: BOD and phosphorus (P). The simple regression between PBDE concentration as a function of log transformed BOD yielded a statistically significant relationship ($p = 0.041, R^2 = 0.599, n = 7$). A multiple regression of PBDE as a function of log transformed BOD and log transformed phosphorus yielded a statistically significant relationship ($p = 0.015$, $R^2 = 87.7\%$ $n = 7$, PBDE $= -187421 + (-11268*LP) + (14461*LBOD)$. The small number of observations in the regressions probably warrants the use of a non-parametric approach such as a robust regression based on ranks. The output from the multiple regression based on rank yielded the following equation; PBDE $= -23436 + (-14448*LP) + (17386*LBOD)$. The coefficients of both the parametric and non parametric regressions are very similar. Since BOD measures the amount of organic compounds in water and PBDES are known to have a high affinity to organic particles, the inclusion of this parameters in the predictive model is not surprising. However, the reason for inclusion of TP as a predictor of PBDEs remains unknown. Prediction of PBDE concentration in environmental matrices has not been conducted often. A study by Oros et al. (2005) detected a statistically significant relationship between PBDEs and TSS in surface water samples ($p < 0.0005$, $R^2 = 0.38$). The results from our multiple regressions explained a higher proportion of the variability of the data (R^2) than the Oros et al. (2005) study. Although the low number of observations associated with the multiple regression leads us to use caution in its interpretation.

References

Anderson TD, MacRae JD (2006) Polybrominated diphenyl ethers in fish and wastewater samples from an area of the Penobscot River in central Maine. Chemosphere 62:1153–1160

Brown FR, Winkler J, Visita P, Dhaliwal J, Petreas M (2006) Levels of PBDEs, PCDDs, PCDFs, and coplanar PCBs in edible fish from California coastal waters. Chemosphere 64:276–286

Environment Canada (2006) Ecological screening assessment report on polybrominated diphenyl ethers (PBDEs). June 2006:16. Available at; http://www.ec.gc.ca/ceparegistry/documents/subs_list/PBDE_SAR/PBDEs_TOC.cfm. Accessed 5 Jan 2010

EPA (2003) Draft Method 1614. Brominated diphenyl ethers in water, soil, sediment, and tissue by HRGC/HRMS. Analytical Methods Engineering and Analysis Division (4303T). Office of Science and Technology US Environmental Protection Agency, 1200 Pennsylvania Avenue Washington, DC 20460

Johnson A, Olson N (2001) Analysis and occurrence of polybrominated diphenyl ethers in Washington state fish. Arch Environ Contam Toxicol 41:339–344

Lalonde B, Garron C, Ernst W (2007) Characterization and toxicity testing of fish processing plant effluent in Canada. EPS-5-AR-07-03

Law RJ, Herzke D, Haard S, Morris S, Bersuder P, Allchin CR (2008) Levels and trends of HBCD and BDEs in the European and Asian environments, with some information for other BFRs. Chemosphere 73:233–241

North KD (2004) Tracking polybrominated diphenyl ether releases in a wastewater treatment plant effluent, Palo Alto, California. Environ Sci Technol 38:4484–4488

Oros DR, Hoover D, Rodigardi F, Crane D, Sericano J (2005) Levels and distribution of polybrominated diphenyl ethers in water, surface sediments and bivalves from the San Fransisco estuary. Environ Sci Technol 39:33–41

Rayne S, Ikonomou MG, Antcliffe B (2003) Rapidly increasing polybrominated diphenyl ether concentrations in the Columbia River system from 1992 to 2000. Environ Sci Technol 37:2847–2854

Sellstrom U, Kierkegaard A, deWit C, Jansson B (1998) Polybrominated dyphenyl ethers and hexabromocyclododecane in sediment and in fish from a Swedish River. Environ Toxicol Chem 17:1065–1072