POLYMERIC FLAME RETARDANTS: POTENTIAL SOURCES FOR LOW MOLECUAR WEIGHT ORGANOBROMINE CONTAMINANTS

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1- Introduction

Long before mankind learned to harness fire as a source of energy, he was horrified by the devastation caused by it. Fire is still a major source of damage to properties and loss of life. Flame-retardants are materials added or applied to a material to significantly increase the fire resistance of that product. Recent advances in technology have resulted in an increase in use of synthetic polymers, electronic equipment, and other ignitable material loads in our commercial and residential habitats. This has drastically contributed to fire hazard. In order to meet fire safety regulations, flame-retardants are applied to combustible materials such as wood, paper, plastics, and textile. Today, there are more than 175 chemicals classified as flame-retardants. Flame-retardants are divided into four major groups: inorganic, halogenated organic, organophosporus and nitrogen based which account for 50%, 25%, 20% and >5% of the annual production respectively[1].

Free radicals (highly oxidizing agents) are produced during the combustion process and are essential elements for the flame to propagate. Halogens are very effective in trapping free radicals, hence removing the ability of the flame to propagate. With high trapping efficiency and lower decomposing temperature, organobromine compounds have become a popular flame-retardant. Since the bromine content is the main ingredient of a brominated flame retardant (BFR), there is no particular restriction on the structure of the backbone. As a result, there are more than 75 different aliphatic, aromatic and cyclo-aliphatic compounds used as brominated flame-retardants. BFRs are divided into three subgroups: additive flame-retardants, which are only mixed together with the other components of polymers; reactive flame-retardants, which are a group of compounds that are chemically bonded into the plastics and polymeric flame retardants where the bromine is placed in the backbone of a polymer. With environmental concerns about the leaching of additive BFRs and a limited possibility to incorporate reactive BFRs, there is a growing trend to use more polymeric BFRs. With a very high molecular weight this class of compounds is less bioavailable. However, there is a growing concern that unreacted monomers or degradation products can become a source of low molecular weight organobromine compounds recently observed in the environment.

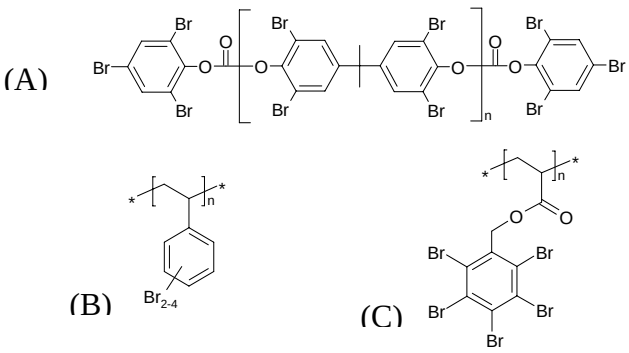

Figure 1: Chemical structure of (A) BC-58, (B) PBS-64, and (C) FR-1025.

BC-58 and PBS-64 are tetrabromobisphenol A carbonate and bromostyrene oligomers respectively (Figure 1A and B). Both are produced by the Great Lake Chemical Corporation. FR-1025 is a pentabromobenzyl acrylate oligomer produced by the Dead Sea Bromine Group (Figure 1C). Their molecular weight ranges between 3500 and 80000 Da. The three BFR oligomers are mainly used in engineering thermoplastics such as polybutylene or polyethylene terephthalates [2, 3].

Material and Methods

Air extracts were provided by Liisa Jantunen and Terry Bidleman from the Metrological Service of Canada, and beluga blubber sample extracts were provided by Michel Lebeuf from Maurice Lamontagne Institute, Department of Fisheries and Oceans.

Thermal stress experiments: Details of the experimental setup and sampling methodology have been already presented elsewhere [4]. Briefly, BFR oligomers were placed in a glass flask and heated to approximately 100 °C. A nitrogen flow was maintained through the system during the experiment and a PUF plug was placed at the exit of the system to collect volatile compounds. PUF plugs were soxhlet extracted with a mixture of dichloromethane (DCM) and hexane (50/50 v/v) for about 20 hours. In parallel, all glass parts of the sampling system were rinsed with DCM. Soxhlet and rinse extracts were then evaporated to obtain a similar final volume in isooctane.

GC-MS analyses: An HP 5890 Series II gas chromatograph coupled to an HP 5989AB mass spectrometer was employed for the examination of the extracts. Chromatographic separation was performed on a 30 m x 0.25 mm i.d. HP-5MS capillary column with helium as the carrier gas The electron capture negative ion (ECNI) mode was used to monitor selected bromide ions at m/z 79 and 81 (ion source T = 175 ºC, ion source P = 1.0 torr, methane as reagent gas). The electron ionization (EI) mode was used to obtain full scan mass spectra of unknown brominated compounds and authentic materials.

GC/HRMS determinations were obtained using an HP 6890 GC coupled with a Micromass Autospec Ultima. Chromatographic separations were accomplished using a 30m x .010 mm i.d. DB5 HT column. The GC injection port was configured for split/splitless injection at a temperature of 280°C. The GC column was maintained at 100°C for 3 minutes, and then ramped at 5°C/min to 320°C. Helium was used as the carrier gas in constant pressure mode. Sample ionization was performed by electron ionization (EI) at an electron voltage ranging from 30 to 40eV depending on the optimization parameters of the instrument. Source temperature was 280°C and the resolving power of the analyzer was at least 10,000. The mass spectrometer was operated in SIM mode using a total of 7 function groups to analyze the suite of BFR compounds.

3- Results and Discussion

At room temperature, the GC-ECNIMS selected ion chromatogram (m/z 79+81) showed a few peaks with low intensity indicating that the PBS-64^{TM} oligomer weakly released volatile brominated compounds. Upon application of thermal stress to the sample a drastic increase of the release of brominated compounds was observed. These compounds were identified as substituted alkyl benzenes or phenols with two to six bromine atoms. For PBS-64 and FR-1025 oligomers, some of the most importantly released compounds were monomer molecules; di- or tribromostyrenes and pentabromobenzyl acrylate, respectively. For BC-58, the monomer unit, tetrabromobisphenol A, was not detected. Other quantitatively

released brominated compounds were tribromophenol and pentabromoethylbenzene (PBEB) for BC-58 and pentabromotoluene (PBT) for FR-1025.

Environmental persistence and potential to bioaccumulate for these compounds were evaluated using EPI SuiteTM [5] and PBT Profiler [6]. Results of these estimations indicated that the majority of these compounds were expected to bioaccumulate in the food chain (Log K_{ow} > 5 and/or BCF > 5000) and to persist in the environment ($t_{1/2}$air > 2 days or $t_{1/2}$water > 182 days or $t_{1/2}$soil > 182 days or $t_{1/2}$sediments > 365 days) as per the Toxic Substances Management Policy of Canada [7]. Of particular interest among these compounds were pentabromotoluene (PBB), pentabromoethyl benzene (PBEB), and penta- and hexabromobenzene (PBB & HBB) which had the highest values for all categories as such they could be considered as the most susceptible to accumulate in biota and persist in the environment. This leads to the question of environmental occurrence for these compounds.

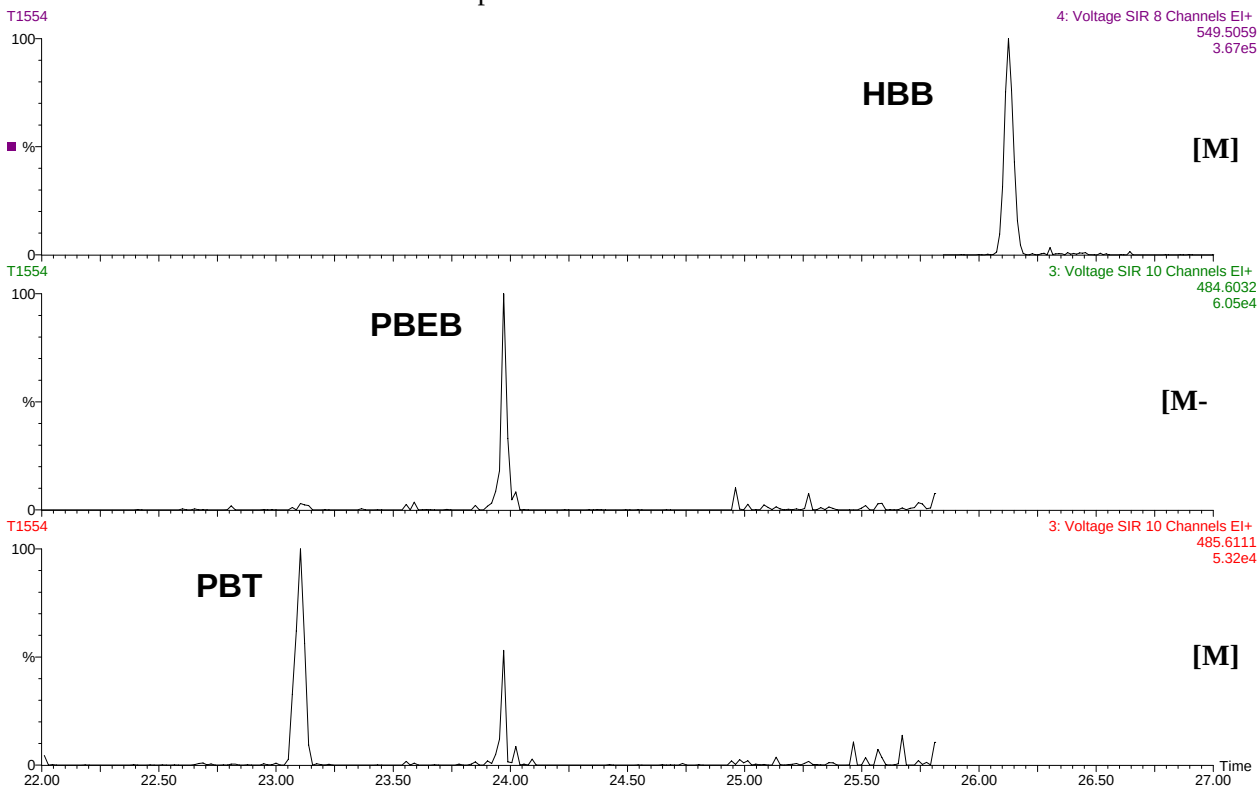

Figure 1. GC/HRMS chromatogram of beluga blubber from St. Lawrence Estuary, indicating presence of pentabromo toluene (PBT), pentabromo ethyl benzene (PBEB) and hexabromo benzene (HBB).

Further investigation indicated that PBB, PBEB and HBB were present in air samples collected in Egbert Ontario and in beluga blubber from the St. Lawrence Estuary. The results from this study indicated that levels of these compounds in these samples were substantially lower than PBDEs. The chromatographic conditions also indicated that PBT and BDE-28 co-eluted under current experimental conditions detecting Br^- (m/z 79 and 81). To eliminate this problem, new experimental conditions using HRMS in EI mode was

developed. Using these experimental conditions, the occurrence of PBT, PBEB and HBB in these samples were confirmed (Figure 1).

A review of literature revealed that limited information is available on these compounds. PBB and HBB have been detected in raw scrap material lots composed of electric and electronic devices in an aluminum recycling plant in Finland [8]. Wensing, showed that PBT could be emitted from TV sets at a rate up to 200 pg/unit/hour [10]. HBB was found in some bottom sediment samples collected during a recent survey of chemicals of concern throughout Japan [11]. Levels, up to 43 ng/g dry weight, HBB was also detected in air samples with a detection frequency of more than 70 % and at levels up to 100 pg/m^3 [11]. HBB however, was not detected in surface water or fish. PBT and PBEB were detected in an air sample collected in Chicago in the summer of 2003. Hoh et al reported a concentration of 520 pg/m^3 for PBEB which was much higher than the total PBDE (tri to hexa PBDEs) concentration which was only 47 pg/m^3 [9]. PBEB was also detected in 2001 Chilton (UK) air samples at an average concentration of 30 pg/m^3 (n=45); three times higher than the average concentration of total PBDEs (tri to hepta PBDEs) [13].

4- Acknowledgements
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