LEACHING CHARACTERISTICS OF HEXABROMOCYCLODODECANES (HBCDs) FROM EXPANDED POLYSTYRENE BUOY IN WATER

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Intrduction

Hexabromocyclododecane (HBCD) isthe second highest-volume BFR used after tetrabromobisphenol-A and before decabromodiphenylether. It is the principal flame retardant in polystyrene (PS) foamsand is used as thermal insulation in the building industry.Technical HBCD is usually a mixture of the three diastereoisomersα, β and γHBCD. Normally, the γ isomer is the mostabundant in commercial mixtures (75 -89%), followed by α and β isomer (10–13% and1–12%, respectively).The different molecular properties (polarity, dipole moment and solubility in water) ofα, β and γ isomers might lead to the differencesobserved in their environmental behaviour.

The release of HBCD into the environment is considered as an issue of global concern.As an additive BFR, HBCD is not covalently bonded to the material into which it is impregnated, leading to the risk of migration out of the product during production,use or disposal[1].Some reports indicate that it is highly toxic to rats and induces cancer[2,3]. HBCD can also affect the normal uptake of neurotransmitters in rat brain[4].Therefore, it is being considered under the framework of StockholmConvention on Persistence Organic Pollutants.

HBCDhas attracted an increasing worldwide attention and,therefore, a vast literature is available on the detection of HBCD in the environmentcaused by the industrial or anthropogenic activities[5-8].However, fascinating point is the presence of HBCD in water, oyster and sediment collected from andnearby aquafarms i.e. non-industrial area (unpublished). Expanded polystyrene (EPS) buoy,a rich source of HBCD,is highly used in Korea for the culture of longline oyster. These observations encouraged us to carry out the leaching studies on EPS buoy. Most of the research undertaken in recent past has been confined with respect to PS litter as a contaminant[9]and HBCD that can leach from PS has still been unexplored as yet.

Leaching is dependent on a number of parameters. Keeping these facts in view, it is imperative to investigate the leaching of HBCD from EPS buoys. The simplest approach to the problem should be to follow the leaching under controlled laboratory conditionsin deionized water at different passage of time. The effect of different parameters such as temperature (15, 28^{0}C), salinity(25, 32‰) and shakingwas also evaluated. In each case, initial and final samples of EPS were used to check the mass difference in HBCD.

Materials and methods

Reagents

Native standards of αHBCD (>98%), βHBCD (> 98%), γHBCD (>98%) and isotope-labeled 2,2',3,4,4',6-hexabromo[$^{13}C_{12}$]diphenyl ether (^{13}C-BDE-139) were obtained from Wellington Laboratories, Inc (Ontario, Canada). The isotope labeled standard of HBCDs (Mix of 3 diastereoisomers$^{13}C_{12}$, 99%) was purchased from Cambridge Isotope Laboratories, Inc (JA, USA). All solvent used throughout the experiment are of capillary GC/GC-MS grade and procured from Burdick and Jackson (MI, USA). The ultrapure water was produced by a MILLI-Q Advantage A10 (France).

Liquid chromatography-tandem mass spectrometry

An Agilent HPLC system (Model No 1200, Agilent Technologies, Waldbronn, Germany), equipped with a triple quadrupole mass spectrometer detector (API 3200 Applied Biosystems from MDS SCIEX, Toronto, Canada), was employed for the identification and quantification. HPLC system consisting of two high pressure pumps with a pressure and flow capability of 9.9 mL/minand automated gradient controller was used to program the elution system. A Zorbax Eclipse C18 analytical column (4.6×150 mm, 3 μm particle size) preceded by a low-dispersion in-line filter (0.25 μm) from Agilent Technologies (USA) were used. The oven temperature was set at 40^{0}C. The HPLC and tandem MS were connected via a Turbo V^{TM} ionization source from AB SCIEX (Singapore). This ionization source can operate as an ESI or APCI interface. Nitrogengas was generated using a

nitrogen generator from Peak Scientific (MA, USA). Analyst 1.4.2. Software was used for system control as well as data acquisition and processing.

Chromatographic conditions

The gradient program for the chromatographic analysis consisted of a binary mobile phase solvent system (A= acetonitrile:methanol in 70%:30% ratio and B=100% methanol).Details of HPLC-APCI/MS/MS analysis can be found elsewhere[10].The mass spectrometer was operated in atmospheric chemical ionization (APCI) negative ion mode.Quantification of each HBCD was carried out by an isotopic dilution technique, The mass spectrometric parameters were optimized for labeledBDE-139 (^{13}C) and then eluted at the same program. BDE-139 (^{13}C)was used for quantitative recovery of internal standards.

Leaching experiment

Laboratory experiments were conducted using known volumes (3L) of Millipore water as such, and or containing different amounts of sea salt (25 and 32‰) placed in glass bottles with a capacity of 5 L. A known amount (~3 g) of detached EPSspherules from buoy (fresh) is kept into the water at room temperature. They were placed as to immerse completely into the deionized water. The amount of leached HBCD was extracted from the subsamples (200 mLof water) collected after a certain interval of time i.e., 1, 6, 12, 24, 48 and 96 h.Under finally optimized conditions, subsamples of 200 mL were filtered on 0.4 µm glass fibre filter paper and fortified with 80 µL of 1 ng/µLlabeled internal standard (I.S.) solution. The fortified samples were then extracted using dichloromethane (DCM, 30 mL×3). The procedure was repeated for getting good recovery.The water samples were stored at 22±1^{0}C unless mentioned otherwise. The leaching profile of the HBCD was followed under different conditions by determining the released concentration in different samples after a definite time period. For calculating mass difference of HBCD in fresh and treated EPS buoy uniform solution method was used. In triplicate analysis, each subsample (~0.03 g EPS in 4 mL DCM) was then spiked with 80 µL of (1 ng/µL) labeled I.S, vortex for 1 min and finally evaporated to dryness under a gentle stream of N_2 gas. Dry extracts were eventually reconstituted with 200 µL of acetonitrile and transferred to 0.4 mL Jini-UniPrep vial filter for instrumental analysis.The concentration of HBCDs is the sum of the α, β and γ diastereomers detected in all samples.

Results and discussion

Leaching of HBCDs from EPS buoy

Concentration of HBCDs in fresh EPS buoy, after treatment and in water at various conditions along with rate constant is presented in Table 1.

Table 1: Concentration of HBCDs in fresh EPS buoy , after treatment and in water at various conditions

HBCDs in fresh EPS buoy: 70±4.9 µg/g				
Variable	**HBCDs in treated buoy (µg/g)**	**Mass difference in HBCD (µg/g)**	**HBCDs in water (Cm in µg/L)**	**k (h^{-1})[a]**
Temperature				
15^{0}C	61.1±2.8	8.9(12.7%)[b]	7.1(10.1%)[c]	0.03
28^{0}C	54.7±4.8	15.3(21.9%)	10.3(14.7%)	0.07
Salinity				
25‰	54±0.2	16.0 (22.9%)	14.5(20.7%)	0.02
32‰	56±2.5	14.0 (20.0%)	11.0(15.7%)	0.11
Shaking				
No shake	58.5±4.2	11.5(16.4%)	10.9(15.6%)	0.70
With shake	56.8±3.0	13.2(18.9%)	11.2(16.0%)	1.74
Buoy				
Part1	56±2.0	14.0(20.0%)	4.7(6.0%)	0.54
Part 2	58.5±4.2	11.5(16.4%)	10.9(15.6%)	0.69

[a]Leaching rate coefficient
[b]Percentage of HBCD lost from EPS buoy during leaching
[c]Percentage of HBCD leached from EPS buoy in water

The leaching profiles of HBCD in water are shown by the Figure 1. The results reveal faster leaching of HBCD initially and thereafter it gradually increases to reach the maximum. The maximum leached concentration from different parts of EPS at different time found in water is 6-15% of total HBCDs per gram of buoy (~5-11 µg/L). The variation in leached concentration affirmed that there is no uniformity in the level of HBCD in a buoy or in different buoys. Nevertheless, γHBCD was the most abundant isomer followed by αHBCD and βHBCD, accounting for 56%, 37% and 7%, respectively, of the total HBCD concentration leached in deionized water at room temperature after 96 hours. Mass balance with EPS also confirms the 16-20% loss of HBCD from EPS buoy into the water in the form of leaching. Considering that releasing of HBCD followsa first-order process, its leaching concentration (C) can be brieflyexpressed as follows:$C = C_m(1-e^{-kt})$, where $C_m$is the maximum concentration of pollutant that can be leached out for an infinite time elapse, and k is the rate coefficient

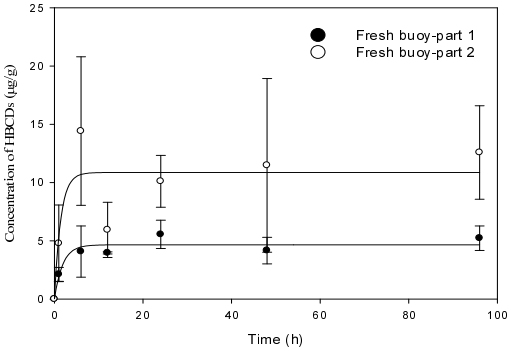

Figure 1. Leaching of HBCDs from different parts of fresh EPS buoy at different time

Effect of temperature

To investigate the effect of temperature on the leaching ofHBCD, studies were carried out at two different temperatures(15 and 28°C) in Millipore water (pH 6.3). The results suggest that there is an exponential increase (Fig. 2) in the concentration of HBCD with time. As expected, the rate of leaching increased with the increase in temperature and the maximum leaching concentration varied from 7.1 µg/L to 10.3 µg/L(Table 1).

Effect of salt concentration

Investigations were conducted at different salt concentrations in water (Fig. 3). It is apparent that the leaching concentration increases with the presence of salt in the water with which it was in contact (Table 1). It may be important to point out that although rate constant is increased with increase of salinity but the leaching concentration is found to maximum at 25‰ salinity than that of 32‰.

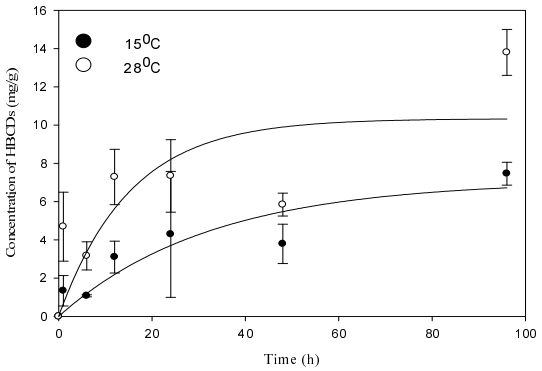

Figure 2.Leaching of HBCDs at different

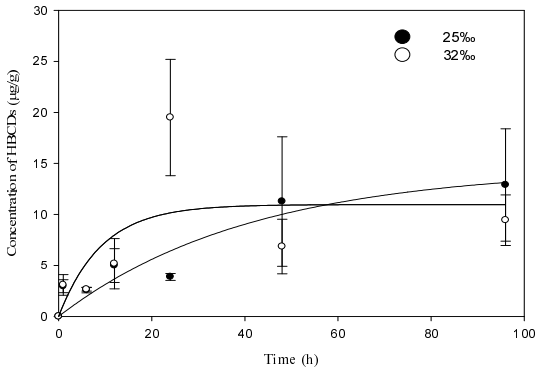

Figure 3. Leaching of HBCDs at different salinity

temperaturesfrom freshEPS buoyfrom fresh EPS buoy

Effect of shaking time

Shaking to the matrix is supposed to affect the leaching of HBCD (Fig 4). The studies carried out in the in controlled condition at laboratory temperaturereveal thatthe maximum concentration released during shaking is almost same with that of sample kept under staticcondition (Table 1). This fact can be verified by the statistical analysis of data in water and treated EPS. There are no statistical differences observed in data of water and treated EPS. The rate constant is increased more than two times in presence of shaking.

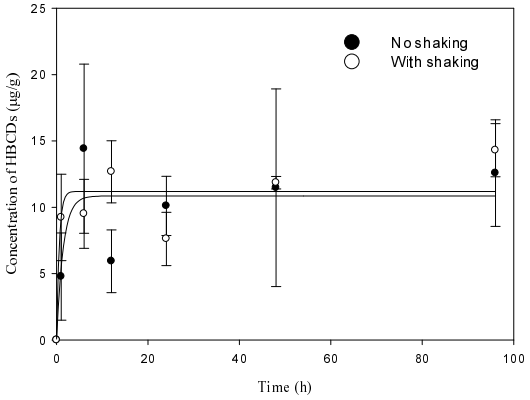

Figure 4. Effect of shaking on leaching of HBCDs

Conclusions

Results show that leaching of HBCD from EPS in water is initially faster reached almost maximum within 24 h and further move slowly to the saturation point. Mass balance with EPS also confirms the release of HBCDsinto the water. Although loss of some mass to air may also be occurred that cannot be ignored. On an average leaching rate increases exponentially with increase in temperature and salinity. Statistical analysis(t-test) also confirms the difference between the analysis of treated EPS at different temperature and salinity. Difference in mean shows slight increase in leaching rate with shaking. These differences were not found to be statistically significant (p> 0.05), in part, due to the high level of variance in replicate observations.The leaching profiles in all these cases follow first order kinetics.

Acknowledgement

The authors would like to acknowledge Korea Institute of Ocean Sciences and Technology for funding the scheme (PE 99153).

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