SOURCES AND PATTERN ANALYSIS OF POLYBROMINATED DIPHENYL ETHERS (PBDEs) IN SEDIMENT OF HANOI WATERSHED

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Introduction

Polybrominated diphenyl ether (PBDEs) are anthropogenic chemicals that have been extensively used as additive flame retardants (FRs) in many consumer and industrial fields, such as furniture, electronic product, textiles, and building materials… as three commercial mixtures Penta-BDE, Octa-BDE and Deca-BDE. The global concern has been increasing toward PBDEs due to their persistent, bioaccumulative properties and potential toxic risk to living organism especially human. With the wide spread of PBDEs into the environment, researchers have reported significant levels of the compounds in many environmental matrices as well as biological samples. Some studies have informed the presence of PBDEs in Vietnam environment such as sediment of Thi Nai Lagoon and soil from its mainland (Romano et al, 2013), indoor dust and air (Tue et al, 2012), rivers and lakes of cities and industrialized areas (Minh et al, 2010).

Hanoi is the capital of Vietnam and the second most populated city of the country. Population of Hanoi in 2012 was approximately 2.9 million for urban district and 6.9 million for the metropolitan region (www.gso.gov.vn). With such a huge population, there is an enormous potential of PBDEs emerging from furniture, electrical devices, dumping sites, etc., which can be released in to the environment through waste water and rain. Our previous work (Thuong et al, 2012) reported a slight accumulation of PBDEs in Hanoi rivers and lakes sediment. Motivated by this previous study, after acquiring the initial assessment of PBDEs contamination level, we conducted chemometrical techniques to determine pattern characteristic of PBDEs in these sediments on the view of statistical analysis, from which possibly sources of PBDEs can be identified and how could they be introduced into study area. Although extensively monitoring for the occurrence of PBDEs will be needed for exactly identify the sources, this study still provides reliable results, which can be used as a reference for regulation of persistent organic pollutants in general, particularly PBDEs in Hanoi.

Materials and methods

Stratified-random sediment samples from some canals and lakes of Hanoi were collected in 2011 and analyzed by Dioxin laboratory (Nguyen Van Cu, Hanoi, Vietnam). The detail analysis method is described elsewhere (Thuong et al., 2012). Briefly, 20g wet sediments were mixed with anhydrous sodium sulfate and spiked with $^{13}C_{12}$-labeled surrogate standards. The samples were extracted by Soxhlet extraction for 16 hours and then purified using a multilayer silica gel column. Prior to instrumental analysis, all samples were spiked with internal standards and concentrated to 50µL.

The emerging levels of the individual PBDE congeners in sediment were assessed for spatial extent and possible sources. Summary statistic and chemometrical approaches were calculated by setting non-detetected values to half of method detection limits. Individual distribution identification was performed to identify distribution characteristic of the data set. From the results of individual distribution identification, a proper correlation test was used to assess the correlations between individual PBDE congeners. Principal component analysis was carried out to infer the potential sources of the compounds. These statistical analyses were performed by using Minitab 16.1 software package for Windows.

Results and discussion

One of the most important things when assessing persistent organic pollutants is their spatial distribution. Figure 1 shows the distribution of seven congeners that were detected in the sediment samples from Hanoi watershed. The congener BDE 47 is the most abundant, following by congeners BDE 99 and BDE 183. All the samples shared similar congener pattern profile, which imply the same emission sources. Potential sources of PBDEs may come from electronic manufacturing industry, e-wastes dumping sites, recycling activities, and domestic waste water, which is often directly introduced into watershed system. The concentration of BDE 99 accounted about 40% of the total seven PBDEs. This is similar to that of commercial product of Penta-BDE (45%), which indicates that leaching of Penta-BDE used in polyurethane and furniture was an important contamination source.

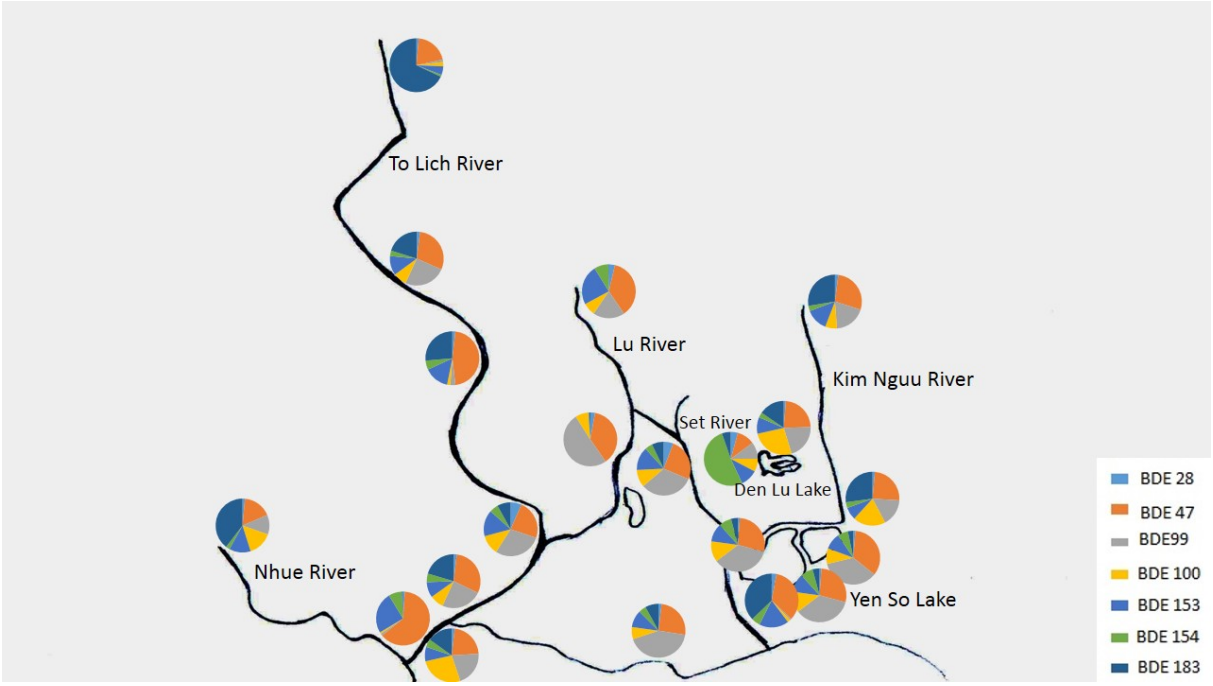

Figure 1. Spatial distribution of seven PBDEs in Hanoi watershed sediment

The individual distribution identification showed that the data set is not normal distributed (P-Value < 0.005). Only Johnson transformation is good enough to convert the raw data into a normal distribution (P-Value = 0.102). To prevent the unintended bias interpretation when assessing the data, no transformation was made and the data was treated as non-parametrical data, using non-parametrical statistical techniques. Spearman's rank correlation analysis was performed and the results are shown in Table 1. Within the individual BDE, all of them demonstrated positive correlation with each other and with total level of seven PBDEs. The correlation coefficient varied from weak to very strong. This indicated that, the mechanisms by which individual congeners were introduced into the investigate area were different. However, despite the difference in emerging mechanisms, there still some interesting results from the relationship of the congeners. BDE-47 was highly correlated with BDE-153 and -154. Possibly, these three congeners came along with each other from potential sources that introduce the pollutants to all of study area. Since BDE-47, -153 and -154 both are present in Penta-BDE mixture, this result consolidated our hypothesis that e-waste was one of the main emission derivation.

Of all the BDE congeners, BDE-47 and BDE-153 had the second and third largest correlation coefficient with the total seven PBDEs. Surprisingly, BDE-28 showed the strongest correlation with total seven PBDEs. This may be due to the degradation of higher brominated PBDEs, which would form BDE-28 (Lei Fang et al, 2008), leading to a strong relationship between level of BDE-28 and total concentration of seven PBDEs.

Table 1. Spearman's rank correlation coefficient for 7 BDE congeners and total PBDEs in Hanoi watershed sediment.

	BDE28	BDE47	BDE99	BDE100	BDE153	BDE154	BDE183
BDE47	0.794						
BDE99	0.635	0.549					
BDE100	0.551	0.562	0.836				
BDE153	0.851	0.927	0.504	0.522			
BDE154	0.628	0.761	0.385	0.44	0.757		
BDE183	0.42	0.402	0.258	0.454	0.386	0.075	
Total 7 PBDEs	0.925	0.875	0.7	0.641	0.881	0.677	0.463

To double check and further interpret the assumption about the sources and distribution characteristics of contaminated BDE congeners, the pattern recognition technique - Principal Component Analysis (PCA) was performed. The screen plot output of PCA analysis suggested that there are three main component contributing to the accumulative level of BDE congeners with significant larger eigenvalue (4.18, 1.78, 0.85 respectively) in comparison with the rest of the components (eigenvalue lower than 0.1). Among the three main principal components, the contribution of each to the total principal components was 59.7%, 25.6% and 12.3% respectively.

Loading plot of first and second component can visualize the different emerging patterns of individual BDE congeners by two possible contamination sources.

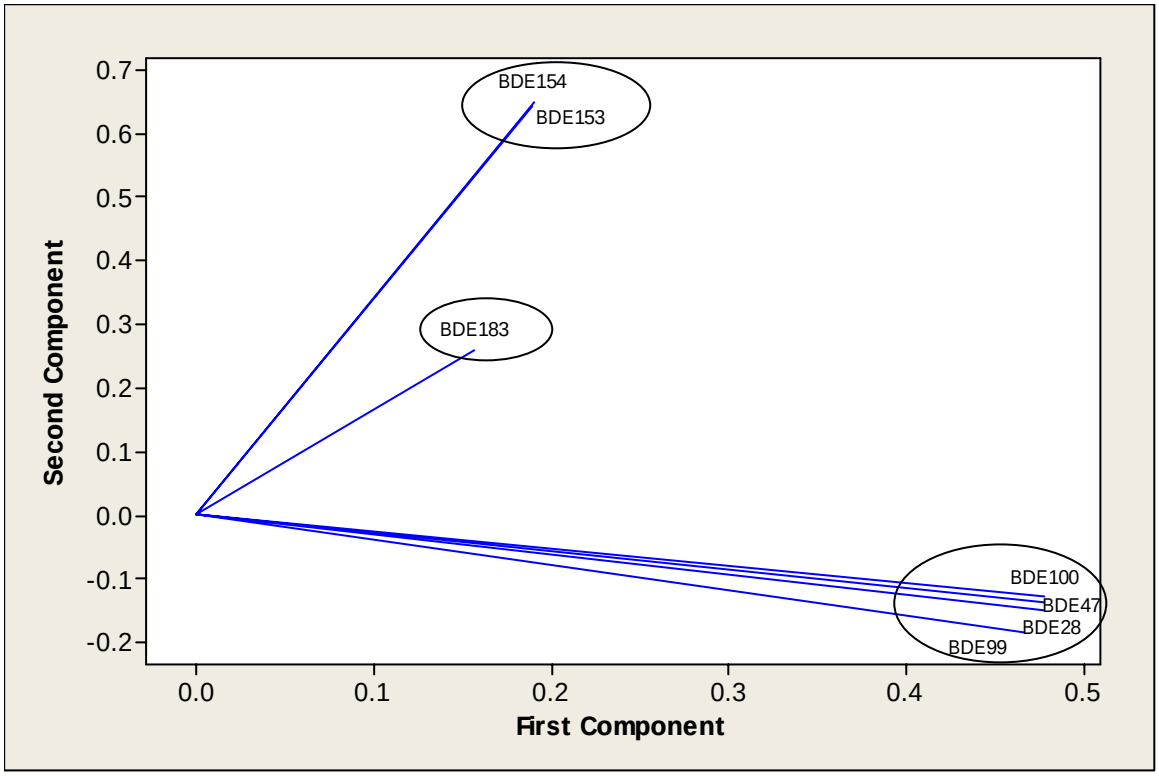

Figure 2. Loading plot of first and second principal component of PBDEs in sediment of Hanoi watershed

All of the coefficients in the first component were positive, which mean all the BDE congeners possibly were introduced by this theoretical source. There are four congeners had similar coefficient and significant larger than the other: BDE-28, BDE-47, BDE-99 and BDE-100. They are tri- to penta-BDE, and included in the main

components of Penta-BDE commercial mixture. We hypothesize that this source came from industrial activities located around the city. The second component consisted of 4 negative coefficients belonging to BDE-28, BDE-47, BDE-99, BDE-100 and three positive coefficients of the other three. This result inferred a different source that contained mainly BDE-153, BDE-154 and BDE-183, but did not have the other four congeners. This led to an assumption of another possible source: commercial Octa-BDE which contains of mostly Hexa-, Hepta- and Octa-BDE. Octa-BDE is commonly used as a flame retardant in the housings of plastic and electronic equipment. The third principal component involved mainly BDE-183 which can be easily release from BDE treated products due to its high volatility. These results suggested that along with pollution from commercial Penta- and Octa-BDE in industrial activities, the released PBDEs from electronic and consumer products, as well as electronic waste accounted a significant amount to the total contaminated levels of PBDEs.

Acknowledgements
This study has implemented in the framework of Dioxin Laboratory Project funded by Vietnam Ministry of Natural and Environment, Bill & Melinda Gates Foundation, and the Atlantic Philanthropies Foundation. This work also was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) (No. 2011-0028723). The authors would like to thank Professor Chang Yoon-Seok and Dr. Pham Thi Ngoc Mai for their help in interpreting the data.

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