POLYBROMINATED DIPHENYLETHERS (PBDEs) LEVEL IN SEDIMENT IN RIVER AND LAKE OF HANOI CITY, VIETNAM

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Introduction

Polybrominated diphenyl ethers (PBDEs) have been widely used as brominated flame retardants (BFRs) in consumer and industrial products, such as textiles, clothing, electric and electronic component, building materials to decrease the fire from their materials. PBDEs include three commercial versions of pentabromodiphenyl ether (penta-BDE), octabromodiphenyl ether (octa-BDE), and decabromodiphenyl ether (deca-BDE). The penta- and octa-products are a mixture composed of several PBDE congeners, while the deca-product is composed almost of deca-BDE[1]. PBDEs have been found at high levels in indoor dust, sewage sludge, and effluents from wastewater. Various PBDEs and their commercial products have also been studied for eco-toxicity in mammals, birds, fish, and invertebrates. Due to their widespread presence in the environment and their reported possible adverse health effects, PBDEs have become the subject of intensive research. PBDEs can reach the environment through leaching during production and application processes, through volatilization and leaching during use. PBDEs are not produced in Vietnam but are concerned issues because their products have been widely used from various consumer products for the decades. However, very few studies have been carried out in Vietnam focusing on PBDEs contamination in rivers and lakes of cities and industrialized areas in Vietnam[2].

The most commonly detected congeners are BDE-28, 47, 99, 100, 153, 154, 183 and 209, which are mainly congeners in the commercial mixtures[1]. Analysis of PBDEs in environmental matrices samples mainly based on gas chromatography-mass spectrometry (GC-MS), working in their electron ionization (EI-MS) or negative ion chemical ionization (NICI-MS). Recently, gas chromatography coupled to tandem mass spectrometry (GC/MS-MS) with EI mode has also been proposed for the analysis of PBDEs at lower concentration, and a few numbers of congeners have been studied from tri- to hepta-BDE, while analysis of highly BDE (particularly deca-BDE) is difficult[3].

This study provide preliminary results to understanding the contamination level of PBDE as well as their potential toxic effect in Hanoi city, the second largest population in Vietnam. This study also validates a highly sensitive, selective method for PBDE analysis based on GC/MS-MS instrument.

Materials and Method

Twenty one surface sediment samples (0-5 cm) from canals and lakes of Hanoi were collected in 2011 using Ekman grab. Sediment samples was homogenized inside the grad and about 200 g was collected in clean polyethylene bags and transported to laboratory and stored at -10^{o}C in darkness until analysis. Moisture content of sediment samples was determined by gravimetric method by drying samples to constant in oven at 105^{o}C for 12 hours. The sampling location has showed in Figure 1.

Wet sediment samples (20 g) were extracted with acetone by sharking a flask vigorously in 60 minutes. The extracts was filtered and separated entirely by water-hexane re-distributor method. Extracts contain PBDE and other organic compounds, which has been spiked with $^{13}C_{12}$-labeled BDE congeners 28, 47, 99, 100, 153, 154 and 183 as surrogate standards (EO-5277, Cambridge Isotope Laboratory, USA). The extracts were concentrated to 1-2 ml before clean up through multi-layer silica gel. The clean up column has been packed from bottom to the top as follow: silica (1g), 2% (w/w) of KOH-silica gel (4g), silica (1g), 44% (w/w) of H_2SO_4-silica gel (8g), silica (2g) and 4 g of sodium sulfate anhydrous. PBDE was eluted by 100 ml of 10 % of dichloromethane in

hexane, and clean up solution was concentrated to 50 µl. The extracts were then added PCB 52 and 138 which used as internal injection standards for determination of recovery efficiency of surrogate standards.

Sample preparation and analysis of PBDEs are carried out according to US-EPA method 1614. Almost of samples has been analyzed by GC/MS-MS (Agilent 7000 triplequadrupole, USA) and DB-5MS (60m x 250µm i.d x 0.25 µm film thickness) capillary column. The temperature program of oven was follows: 90^{o}C for 1 minute, 90^{o}C to 320^{o}C at 20^{o}C/min, 320^{o}C for 18 minutes; a PTV solvent vent mode of injection was follow: 88^{o}C for 0.01 minute, 88^{o}C to 325^{o}C at 600^{o}C/min and keep in 5 minutes. The ion source temperature was 280^{o}C and the MS1 and MS2 were 150^{o}C. In MS-MS mode, for native PBDEs the [m+2] was selected for precursor ion of tri-BDE. The corresponding [m+4] ion was chosen for penta-BDE and hexa-BDE, while [m+6] was selected for hepta-BDE[4].

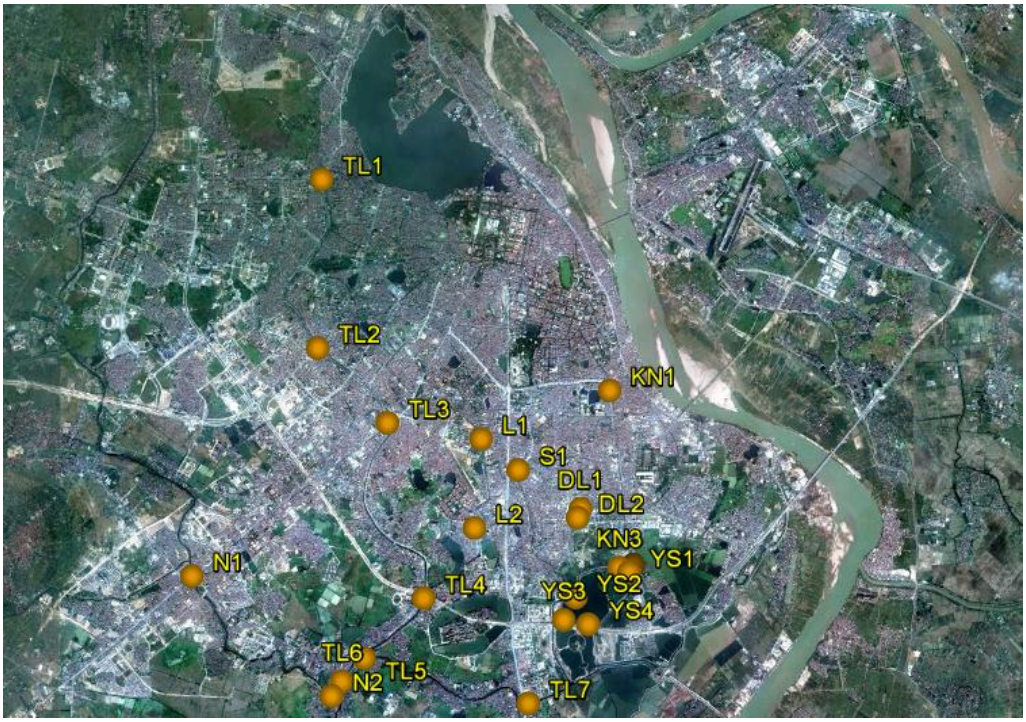

Figure 1: Map of sampling location in Hanoi city

Results and discussion

The concentration of the PBDE congeners in sediment of the Hanoi sewer and lake systems are given in Figure 2. Seven individual PBDE congeners, including BDE 28, BDE 47, BDE 99, BDE 100, BDE 153, BDE 154 and BDE 183 were detected in sediment samples. Although higher PBDE such as BDE 206, BDE 207, and BDE 209 have been considered as one of the largest PBDE contaminants in environment, detection of deca-BDE has not been done due to difficulty with limit of detection on GC/MS-MS. Therefore, sum of other lower BDE congeners will provide preliminary assessment on PBDEs contamination in Hanoi. The sum of 7 individual PBDE congeners was varied from 0.02 to 17.5 ng/g dry weight. The concentration of Σ7BDE in river sediment was varied depending on the sampling locations, 0.02-0.76 ng/g in the To Lich river, 0.14-0.17 ng/g in the Nhue river, 0.38-2.21 ng/g in the Kim Nguu river, 0.75-17.5 ng/g in the Lu river, and one sample collected in Set river was 0.81 ng/g. Beside river sediment, the concentration of Σ7BDE in lake sediment were 0.03-0.04 ng/g in the Den Lu lake, and 0.14-0.26 ng/g in the Yen So lake. The lowest concentrations were also found at Den Lu lake, where the sediment was primarily soil. All the collected samples contained PBDE and the highest concentration was observed at L3 site (17.50 ng/g dry wt), where received wastewater from high populated in Hanoi.

The PBDE concentration found in Hanoi sediment samples in this report were compared with other measurements in sediment from other countries. The PBDE concentrations, except for BDE 209 had measured in sediment from Osaka Bay, Japan range from 8-352 ng/g for 6 congeners[5], 0.04-94.7 ng/g for 9 congeners in Pearl River Delta, China[6], and 0.6-17.6 ng/g for 5 congeners in Netherlands[7]. These results were demonstrated that a slightly accumulation of Σ7BDE in sediment in river and lake of Hanoi.

Figure 3 showed the congener profile of PBDE in Hanoi sediment samples, which BDE 47 was predominant congener followed by BDE 99 and BDE 183. This congeners profile agrees well with observation in sediments in other previously report in China and American Great Lakes[6,8]. The BDE 47 and BDE 99 were the most abundant in commercial penta-BDE and octa-BDE mixtures, which were banned from all products in Euro and several states of America[8]. The congener profile of PBDE in sediment samples found can be explained by the leaching of PBDE from consumer products during use.

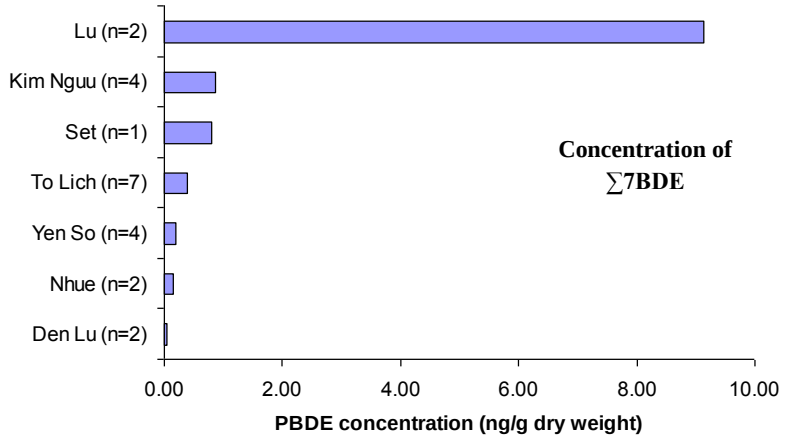

Figure 2: The PBDE concentration of Hanoi sediment samples

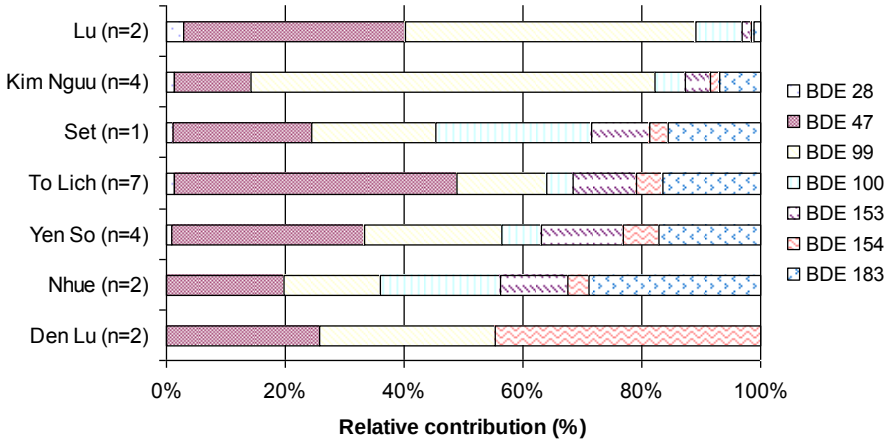

Figure 3: The PBDE congener profile of the Hanoi sediment samples

Acknowledgements

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References

1. Hites, R.A. (2004); *Environmental Science and Technology*. 38: 945–956.
2. Nguyen Hung Minh, Tu Binh Minh, Tomohiko Isobe, Shinsuke Tanabe. (2010); *5th International Symposium on Brominated Flame Retardants – BFR 2010, Kyoto, Japan.*
3. Catherine Pirard, Gauthier Eppe, Anne-Cécile Massart, Edwin De Pauw, Jean-Francoi Focant. (2005); *Organohalogen Compounds.* 67: 171-174.
4. *Agilent Technologies*. (2005); Determination of polybrominated diphenyl ethers (PBDEs) in sediment and sewage sludge.
5. Ohta, S., Ishizuka, D., Nishimura, H., Nakao, T., Aozsa, O., Shimidzu, Y., Ochiai, F., Kida, T., Nishi, M., Miyata, H. (2002); *Chemosphere*. 46: 689-696.
6. Mai, B., Chen, S., Luo, X., Chen, L., Yang, Q., Sheng, G., Peng, P., Fu, J., Zeng, E.Y. (2005); *Environmental Science and Technology*. 38: 3521-3527.
7. De Boer, J., Wester, P.G., Van Der Horst, A., Leonards, P.E.G. (2003); *Environmental Pollution*. 122: 63-74.
8. Susan D. Shaw, Michelle L. Berger, Diane Brenner, Kurunthachalam Kannan, Nina Lohmann, Olaf Päpke. (2009); *Science of the Total environment.* 407: 3323–3329.