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GC/ion Trap MS Method Development and Applications for the Analysis of Polybrominated Diphenyl Ethers in Environmental and Biota Samples

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ABSTRACT

Investigations on the concentrations and congener pattern distributions of polybrominated diphenyl ethers (PBDEs) in environmental samples (sediment, ash, and soil) and fish samples collected from Guiyu were conducted. Guiyu is a traditional rice-growing village located in southeastern Guangdong, China. In recent years, however, the village has turned into an intensive electronic-waste (e-waste) recycling and dumping site. Incomplete combusting of e-waste, dismantling and dumping of processed materials have been identified as the major sources of various toxic chemicals including PBDEs. Analytical methods were developed and applied for the determination of PBDEs in the environmental and biota samples. Samples were prepared by using Soxhlet extraction and cleaned-up with multiple-step chromatographic columns. PBDEs were analyzed by gas chromatography coupled with ion trap mass spectrometry for mono- to hepta-BDEs and quadrupole mass spectrometry for deca-BDE. The method performance was evaluated with the analyses of quality control samples and certified reference material with different calculation range, and with the recoveries of ^{13}C-labeled internal standards. The obtained recoveries ranged from 75 to 125% with a relative standard deviation of lower than 10% for the targeted PBDE congeners.

Ash from e-waste burning field is one of the contamination sources because ash could be deposited in local soil and river or transported to remote locations. Total PBDE concentrations were detected with the range from 2379 to 6238 μg/kg (dry weight) in the ash samples collected from a largest open burning site and from 247 to 1025 μg/kg in soil samples collected from different locations close to the open burning site. BDE–209, –183, –153, –99, and –47 were detected with the highest

concentrations in the ash and soil samples. The data of the PBDEs concentrations and congener patterns in both ash and soil samples indicated that PBDEs contamination in soil might be resulted from the e-waste burning.

Total PBDEs concentrations ranged from 4.43 to 16.1×10^3 μg/kg and 55 to 445 μg/kg (dry weight) in bank and bottom sediments, respectively, from Nanyang River where e-wastes were disposed. PBDEs were detected at levels of 51 to 365 μg/kg in bottom sediment from Lianjiang River (Guiyu) that is located next to a residential area, compared to the PBDEs concentrations of 16 to 21 μg/kg in the bottom sediment samples collected from Lo Uk Tsuen (Hong Kong) that received the wastewater discharged from a vehicle repairing workshop. No PBDEs were detected in sediment from Mai Po Marsh Pond (Hong Kong) that was served as a reference site. The obtained results indicated that open burning and dumping of e-waste are the major causes of PBDEs contamination. Different congener pattern profiles were observed in sediments from various sampling sites, with BDE–47 as the predominant congener, followed by BDE–99, –153, –183, and –209.

The mean concentrations of total PBDEs in mixed muscles of tilapia (*Oreochromis spp*) from Lianjiang River were 115 ng/g wet weight (ww) and 4.1 ng/g ww in fishes from Lo Uk Tsuen. The highest PBDEs concentrations were obtained in liver tissues (2.70×10^3 ng/g ww), followed by abdomen muscle (1.09×10^3 ng/g ww) of bighead carp (*Aristichthys nobilis*) collected from Nanyang River. The total PBDEs concentrations in fishes showed the following trend: grass carp<mud carp <crucian carp<silver carp<carp. PBDEs concentrations in the abdomen, back and tail muscles of carp were 766, 458 and 530 ng/g ww, and 53, 52, 45 ng/g ww in grass carp, respectively. The PBDEs congener concentrations in muscles correlated well with their lipid contents. BDE–47 and BDE–28 were the

most abundant congeners followed by BDE–17, –15, –66, –154 and –153 detected in the fishes collected from Guiyu. A significant correlation of PBDEs concentrations between sediment and muscle of fish was observed.

Estrogenic affect were used to investigate for the individual PBDEs including BDE–28, –47, –99, –153, –154, –183, –209 and the commercial product DE–71. Results indicate PBDEs may have weak or moderate binding affinity to receptor (estrogenic or EROD) or weak inducing the *umu* operon. PBDEs were found inactive at all stages of signal transduction and expression. No significant mutagenicity and carcinogenicity for individual PBDEs were observed in SOS/*umu* assays.

Because BDE–209 may be debrominated to more toxic low brominated congeners, its absorption, metabolism and toxicokinetics in Japanese medaka (*Oryzias latipes*) were studied. Japanese medaka of d-rR strain was continually exposed to BDE–209 (from 1 ng/L to 100μg/L) for 15, 30 and 60 days by using a flow-through system. Upon the completion of experiments, the fish weights were measured and the PBDEs concentrations were determined. In general, the final weights of the whole fish, the liver of the fishes treated with BDE–209 decreased. The gonads of male fishes also had the higher weight, while the female gonads had lower weight. PBDEs concentrations exponentially increased for the fishes exposed to 10 and 100 μg/L. Total concentrations of PBDEs (tri- to hepta-BDEs) ranged from 42.4 to 697 ng/g ww and BDE–209 was 8.19 to 354 ng/g ww in muscle tissues, indicating that significant debrominated metabolism occurred during the BDE–209 exposure experiments. BDE–209, –155, –47, and –99 were identified as the predominant congeners. Toxicokinetic study indicated that the half-life of BDE–209 ranged form 16.5 to 19.4 days under the continually flow-through condition.

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CHAPTER I. INTRODUCTION