OCCURRENCE OF BROMINATED FLAME RETARDANTS IN FISH AND AIR SAMPLES FROM THE PHILIPPINES

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Introduction

The occurrence of halogenated persistent organic pollutants in the environment has increased over the years due to industrialization. The class of compounds called polybrominated diphenyl ethers (PBDEs) is of particular interest because human exposure to these compounds has been linked to adverse health effects, including disruption of the endocrine system, neurodevelopmental delays, and carcinogenic effects. The PBDEs are mixed into polymers for use as flame-retardants in products such as electronic circuit boards and cases, textiles, vehicles, synthetic building materials, and carpeting. PBDEs are easily leached from these products and are released into the environment. PBDEs are persistent, bioaccumulative, and can be transferred from mothers to offspring through the placenta and breastfeeding, posing risks to the fetus and developing children. It is anticipated that electronic wastes may increase in developing countries, like China, India, Pakistan, Vietnam, and the Philippines, according to the United Nations Environment Program. Most of the recycling in these countries is happening in substandard facilities not equipped to manage hazardous substances. As such, PBDEs may be released into the Asian environments at unprecedented amounts. Considering that fish is a major part of the Filipino diet, assessment of the levels of PBDEs in the Philippine environment and food sources is warranted.

Human exposure to PBDEs is mainly through inhalation of PBDE-containing dust particles, as well as ingestion of contaminated food products such as fish. This presentation will focus on the results of analysis of local Philippine fish, and dust particles, specifically PM_{10} [Particulate matter, 10 microns or less], collected from the Philippines. The PM_{10} are very small solid particles in the air that are of particular concern because these particles are easily inhaled and can be readily absorbed into the lungs, introducing contaminants associated with dust particles into the human body. The objectives of this research are: (1) to assess the current levels of PBDEs in commonly consumed fish in the Philippines, and (2) to determine the changes in concentrations of PBDEs in PM10 samples collected from the air near the Manila Observatory for over several years.

Materials and methods

We purchased fish samples from the local grocery stores in Manila and from the Farmer's Market in Quezon City, Philippines. The fish were ground, and extracted by Soxhlet™ Extraction for 18-24 hours using 50/50 methylene chloride/hexane solvent mixture. A surrogate mix, Brominated Flame Retardants Labeled Compound Solution (BFR-LCS), containing 16 mass-labeled ^{13}C-BDE congeners was spiked into the ground fish samples prior to extraction, clean-up, and analysis to allow quantification by isotope dilution mass spectrometry. Air samples from Metro Manila were collected using the MiniVol™ portable air sampler configured to collect PM_{10} in filters for over 12-hours to determine the PBDE concentrations in these particles. The filters were extracted by ultrasonication, and the extracts were analyzed for PBDEs using gas chromatography with tandem mass spectrometry (GC/MS/MS).

Analysis was carried out using a Trace GC Ultra coupled to a TSQ Quantum triple quadrupole mass spectrometer (GC/MS/MS). The GC was equipped with a Phenomenex ZB-5ht capillary column, 0.25 mm i.d., 0.10-µm film thickness, and 15 m length. The GC was equipped with a programmable temperature vaporization (PTV) injector, and ionization was achieved by electron impact. The mass spectrometer was operated in selected reaction monitoring mode (SRM) using two transitions, with nitrogen as the collision gas. The MS/MS collision energy and collision gas pressure were optimized for each compound individually, for identification and quantification purposes.

Results and discussion

Detectable amounts of PBDEs were found in all fish samples analyzed, confirming our hypothesis that Filipino's are constantly exposed to these chemicals because fish is in the daily diet of every Filipino. These levels are much higher than the PBDE levels typically found in fish species from the United States. The levels of PBDEs in fish with higher lipid content (e.g. tuna belly) was noticeably higher than the levels in fish with lower lipid (e.g. yellow fin tail). While these PBDE levels are generally not harmful to adults, these concentrations can cause neurological effects to young children when exposed to these chemicals through consumption of breastmilk from mothers who have accumulated these chemicals from long-term consumption of fish.

Air samples from Manila had high levels of PM_{10}. The PM_{10} particles are less than 10 microns in diameter, which are easily inhaled and can be readily absorbed into the lungs. As a result, PM_{10} can cause significant health effects, particularly for the elderly and infants, people with asthma and other respiratory diseases. PBDEs tend to accumulate in PM_{10} in the air. Therefore, in addition to the respiratory effects of PM_{10} they may cause harmful effects from PBDE introduction into the body. Archived samples from year 2002, 2006, 2007 that were collected from the Manila observatory showed high concentrations of PBDEs, ranging from 2000 ng/g to 5000 ng/g of PBDE 47. The findings suggest that people in Manila are particularly exposed to PBDEs through ingestion of dust particles in the form of PM_{10}.

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