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CHLORINATED BENZENES IN FISHES FROM DONGTING LAKE

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Introduction

Chlorobenzenes (CBs) are of worldwide concern due to their persistence, toxicity, bioaccumulation,and long-range transport. Hexachlorobenzene (HCB) and pentachlorobenzene (PeCB) are listed as persistent organic pollutants (POPs) by the United Nations Environment Program (UNEP) (SCPOP, 2009). CBs production in China accounts for more than 50% of the worldwide CBs production. The production of 1,2-dichlorobenzene (1,2-DCB), 1,4-dichlorobenzene (1,4-DCB) and 1,2,4- trichlorobenzene (1,2,4-TCB) in China was 12000, 30000 and 1000 tons in 2003, respectively (Zhang and Lu, 2005). HCB has never been used as pesticide in China, but it was still produced as an intermediate of pentachlorophenol in Tianjin Dagu Chemical Company until 2003 with a production quantity of about 2000 tons/yr (Wei et al., 2007). CBs have been detected in water, sediment, soil and sewage sludge (Wang et al., 1995; Wei et al., 2007; Zhang et al., 2005; Zhou et al., 2009). However, reports on CBs in aquatic organisms-especially the aquatic organisms in typical epidemic areas of schistosomiasis prevalence in China-are lacking.

The release of CBs from the production and use of Sodium pentachlorophenate (Na-PCP) has been identified as one of the most important sources. Dongting Lake is the second largest fresh water lake of China, which is also an area with most widely distributed oncomelaniahupensis and has the most severe schistosomiasis epidemic situation in China. Na-PCP has been sprayed as molluscicide in Dongting Lake from 1960s to 1990s, it was estimated that over 9.8×106 kg of Na-PCP had been devoted into the lake; CBs were also carried into the lake with using of Na-PCP. The aims of this study were to investigate current contamination status, distribution of CBs in fish from Dongting Lake.

Materials and Methods

Sixty-eight fish samples belonging to three species were collected from the Dongting Lake in November 2012. Thirty crucian carp were grouped into five muscle, two brain, two gonad and two kidney samples. Eight yellow catfish were grouped into two muscle, one brain, one gonad and one kidney samples. Thirty catfish were grouped into five muscle, two brain, one gonad and two kidney samples. The samples were frozen, dried and ground into powder in a mortar and then passed through a 20 mesh sieve for subsequent analyses. 5 g of the residue from each sample was mixed with 2 g activated diatomite, introduced into pre-cleaned stainless steel cells (34 mL) and extracted with an accelerated solvent extractor (ASE) 300 instrument (Dionex, CA, USA) using n-hexane/methylene chloride (1:1, v/v) solution. 10 ng of TMX, PCNB, and PCB209 were added to each sample as surrogate congener standards.

Chemical analysis was performed using an Agilent 6890/5975 in combination with a capillary VF-5-MS (5% phenyl/95% methyl silicone, 15 m, 0.25 mm i.d., 0.1 μm film thickness, Varian, USA). The column oven temperature was programmed to increase from 90°C (initial time: 1 min) to 250°C at a rate of 4°C/min, then from 250°C to 300°C at a rate of 25°C/min, where it was held for 5 min. The GC injector temperature was maintained at 260°C, with the temperatures of the MS ion source and the transfer line kept at 230°C and 250°C, respectively. The carrier gas was helium, which was applied at a constant flow rate of 1.5 mL/min. Samples (of 1 μL) were injected in splitless mode with a solvent delay of 6 min. The mass spectrometer was operated in EI mode for analysis of CBs. A solvent blank and a procedural blank were inserted for every batch of ten samples to ensure that the samples and the analysis process were free of contamination. Limits of Detection (LOD) of targeted compounds were defined as three times the signal to noise (S/N) ratio and ranged from 0.32 to 0.68 ng/g lw for CB congeners. Spike recoveries for CBs (at 20 ng/g) ranged from 42.70 to 121.10%, while those for TMX, PCNB, and PCB209 ranged from 70.2 to 91.7%, 80.4 to 105.3%, and 90.5 to 111.2%, respectively. Triplicate analyses of six diluted standard solutions (5, 10, 20, 50.0, 100.0 and 200.0 ng/ml for CBs) were performed for each selected standard mixture. Multi-level calibration curves were constructed for quantification and good to excellent linearity ($r2 > 0.99$) was achieved.

Results and Discussion

Concentrations of CBs in fish

Concentrations of ΣCBs in 3 species of fish samples are summarized. The concentrations of CBs in muscle were ranged from 2731.5 (yellow catfish) ng/g lw to 7811.2 (catfish) ng/g lw. 1, 3-dichloroben, 1,4-dichloroben, 1,2-dichloroben and HCB were the dominant CB congeners in muscle samples of 3 species fishes. Concentrations of CBs in brain, gonad and kidney were ranged from 2423.2 (crucian carp) to 3329.6 (catfish), 2557. 9 (catfish) to 4640.1(yellow catfish) and 1628.1 (yellow catfish) to 4667.8 (crucian carp) ng/g lw, respectively. 1,3-dichloroben, 1,4-dichloroben and 1, 2-dichloroben were the dominant CB congeners in brain (accounting for 98.4% to 99.9% of the total CBs), gonad (accounting for 77.6% to 95.5% of the total CBs) and kidney (accounting for 93.5% to 99.8% of the total CBs). CBs from the production and use of Sodium pentachlorophenate (Na-PCP) has been identified as one of the most important sources, which should explain that the high concentration of CBs could be found in organs of fishes from Dongting Lake.

Potential risk assessment

According to the risk assessment information system (US EB/OL, 2009), the estimated cumulative cancer risk for the local residents consumed fish from Dongting Lake were 1.63×10-6 (crucian carp), 1.26×10-6 (yellow catfish) and 1.51×10-6 (catfish), respectively, which is slightly higher than the risk of 1 case per 1,000,000 people generally recognized as acceptable in the United States (U.S. EPA, 2000). It is important to note that many uncertainties were associated with the risk assessment performed in this study. Therefore, caution must be made when interpreting the results presented here. For example, this investigation did not have an opportunity to take into account the potential difference in cancer risks among the various age groups, or the POPs from other foods. Cancer can occur for many different reasons not necessarily linked to the exposure to environmental pollutants. Furthermore, binding to the organic matters may increase or decrease a chemical's environmental persistence or availability for bioaccumulation; or decomposition may occur, which can produce metabolites that may have significantly different properties than those of the parent compound. These chemical and biological interactions are likely to occur in a highly complex system.Despite the considerable uncertainties associated with the cancer risks estimated in this study, the risk assessment performed here per se is considered to be very useful in determining the overall magnitude of a cancer threat. It is almost without doubt that when the cumulative risks for the three species of fish are all slightly exceeding 1 case per million, some consumption advisories should be in place to protect the local residents from further exposure to pollution that may lead to the development of cancer.

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