OYSTER AND BLUE MUSSLES AS BIOINDICATORS IN THE CHINESE BOHAI SEA: POLYBROMINATED DIPHENYL ETHERS, POLYCHLORINATED BIPHENYLS, AND ORGANOCHLORINE PESTICIDES IN MOLLUSKS

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Abstract

Seven species of mollusks including bivalve and gastropod samples (114 samples) were collected in summer of 2006 and 2007 to evaluate the spatial patterns of polybrominated biphenyl ethers (PBDEs), polychlorinated biphenyl (PCBs), and organochlorine pesticides (OCPs) and select appropriate bioindicators for the organohalogen compound pollutions in the coastal water of the Chinese Bohai Sea. Compared with other species, Oyster and blue mussels possess higher lipid contents and the concentrations of OCPs and PBDEs in these two were also found to be higher than other mollusks. Principal component analysis and correlation analysis on the relationships between concentration levels relevant to the physiological and environmental factors suggest that *Crassostrea talienwhanensis* (Oyster, Ost) and *Mytilus edulis* (Blue mussel, Myt) can be used as potential bioindicators of pollution by OCPs, PCBs, and PBDEs in the Chinese Bohai Sea.

Introduction

Persistent organic pollutants (POPs) are of great environmental and health concern during the past decades. Organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) have been targeted for ultimate elimination by the Stockholm Convention. Polybrominated diphenyl ethers (PBDEs) are considered as the next generation of POPs to be included into the treaty, due to their similarities to the banned chemicals in regards to in health effects as well as their ubiquitous presence in the environment (1).

Aquatic or marine organisms are always used as bioindicator to elucidate the distributions of POPs both on global and regional scale (2). As water-respiring species, mollusks have unique characteristics as bioindicators. Their elimination of chemicals with Kow > 10^5 is sufficiently slow, which cause bioaccumulation of POPs in organisms (3). Also, they have a sessile lifestyle. Therefore, mollusks as filter feeders are sensitive to indicate local POPs contamination.

The present work is a comprehensive investigation of OCPs, PCBs, and PBDEs in selected mollusks collected from coastal water of the Chinese Bohai Sea in 2006 and 2007. The objective is to select the most suitable mollusk

species as bioindicators of OCPs, PCBs, and PBDEs as well as to examine the temporal trend and spatial distributions of these POPs in the Bohai Sea.

Environmental Section

Mollusks were collected from nine coastal cities along the Bohai Sea including Dalian (DL), Yingkou (YingK), Huludao (HLD), Qinhuangdao (QHD), Tianjin (TJ), Yangkou (YangK), Penglai (PL), Yantai (YT), and Weihai (WH). The sampling was carried out in a period from late July to early August in each year of 2006 and 2007. Seven species of mollusks (*Rapana venosa* (Rap), *Neverita didyma* (Nev), *Scapharca subcrenata* (Sca), *Mytilus edulis* (Myt), *Amusium* (Amu), *Meretix meretrix* (Mer), *Crassostrea talienwhanensis* (Oyster, Ost)) were collected and identified including 59 samples in 2006 and 55 samples in 2007. Sample pretreatment, instrumental analysis, quality assurance and quality control, and quantification of the data followed our previously established methods (4, 5) with minor modifications. OCPs including hexachlorobenzene (HCB), α-, β-, γ-, δ- hexachlorocyclohexanes (HCH), *o, p'*-DDE, *p, p'* –DDE, *o, p'* –DDD, *p,p'* -DDD, *o,p'*-DDT, and *p,p'*-DDT were analyzed using Agilent 6890A gas chromatography equipped with a ^{63}Ni electron capture detector. PBDEs and PCBs results were analyzed by isotope dilution method using Agilent 6890 gas chromatography coupled with Waters Micromass high-resolution mass spectrometer (HRMS) (Manchester, UK). 14 PBDE congeners (BDEs 17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190, and 209) and 25 PCB congeners including 12 coplanar congeners (CBs 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, and 169), six indicator congeners (CBs 28, 52, 101, 138, 153, and 180), and other congeners (CBs 3, 15, 19, 202, 205, 208, and 209) were analyzed.

Results and Discussion

HCHs. Concentrations of ∑HCH (the sum of HCHs and HCB) in the mollusks collected ranged from 0.56 (Nev, TJ) to 99.5 ng/g (Sca, WH) in 2006 samples and from below detection limit (BDL) to 62.7 ng/g (Mer, TJ) in 2007. The concentrations of HCHs were in the following order: *β*-HCH > *δ*-HCH > *γ*-HCH > *α*-HCH. The ratios of *α*-/*γ*-HCH 0.76 (2006) and 0.52 (2007) in mollusks suggested that new sources of the lindane formulation are still being transported into the Chinese Bohai Sea.

DDTs. As the dominant contaminant group, the sums of DDTs (∑DDT: includes the concentrations of *o,p'*-DDE, *p,p'* –DDE, *o,p'* –DDD, *p,p'*-DDD, *o,p'*-DDT, and *p,p'*-DDT) were much higher than ∑HCH in Bohai Sea mollusks. The concentrations of ∑DDT ranged from 1.79 (Rap, HLD) to 521 ng/g (Ost, TJ) in 2006 and from 7.95 (Sca, BDH) to 578 ng/g (Ost, WH) in 2007. No obvious temporal trend of ∑DDT concentrations in mollusks in Bohai Sea was found from 2002 to 2007 by comparing the data obtained in this work with that reported previously (4). Higher concentrations were found for the isomers *p,p'* –DDE, *p,p'* -DDD, and *p,p'*-DDT than their respective o,p isomers. The average ratio of ∑ (DDE+DDD)/ ∑DDT in mollusks collected in 2006 and 2007 was 7.08 (2006) and 4.81 (2007), respectively. The decreasing proportion of DDT isomers implied that there has been no recent input of DDTs to this area.

PCBs. PCB concentrations in mollusks were far lower than OCP concentrations and varied depending on the sampling sites and mollusk species. The sum of all 25 PCB congeners (∑PCB) ranged from 0.34 (Nev, HLD) to 29.9 ng /g (Nev, WH) in 2006 and from 0.46 (Sca, DL) to 11.9 ng/g (Nev, YangK) in 2007. The contamination levels of

∑PCB in this study area were at the low end of the Asian coastal waters range.

PBDEs. PBDEs were detected in all mollusks species. The sum of tri- to hepta-BDEs congeners (∑PBDEs) ranged from 0.11 (Nev, HLD) to 60.9 ng/g (Myt, YT) in 2006 and from 0.04 (Mer, TJ) to 4.39 ng/g (Myt, PL) in 2007. Furthermore, two batches of mollusks samples collected from 2003 and 2005 were also analyzed for the investigation of PBDEs concentrations. Except for the case of Myt, no obvious temporal trends of ∑PBDE in mollusks collected from the Chinese Bohai Sea were found from 2003 to 2007.

PCA was conducted for the sum of HCHs, DDTs, PCBs and PBDEs in mollusks collected in 2006 and 2007 (Figure 1). Compared with the loading and score plot, the distribution of the concentrations of organohalogen compounds in Ost was similar to the distribution of the sum of HCHs, DDTs, PCBs and PBDEs in mollusks.

The results proved that different mollusks showed various abilities to accumulate OCPs, PCBs, and PBDEs. Bivalves, oysters (Ost) and blue mussels (Myt) have been widely used as sentinel species for indicating the levels of pollution in coastal environments (6) due to their sessile lifestyle, low position in food chain, easy sampling procedure, tolerance towards a wide range of salinity and high accumulation capability for numerous pollutants. In this study, Myt and Ost showed high concentrations of ∑DDTs and ∑PBDEs. Based on the PCA results and the relationship between pollutants in mollusks and sediment, it is judged that Ost and Myt are the most sensitive bioindicator in indicating the contamination status of organohalogen compounds in the Chinese Bohai Sea. This study also provides valuable information on the current levels of organohalogen compounds over space and time in this area.

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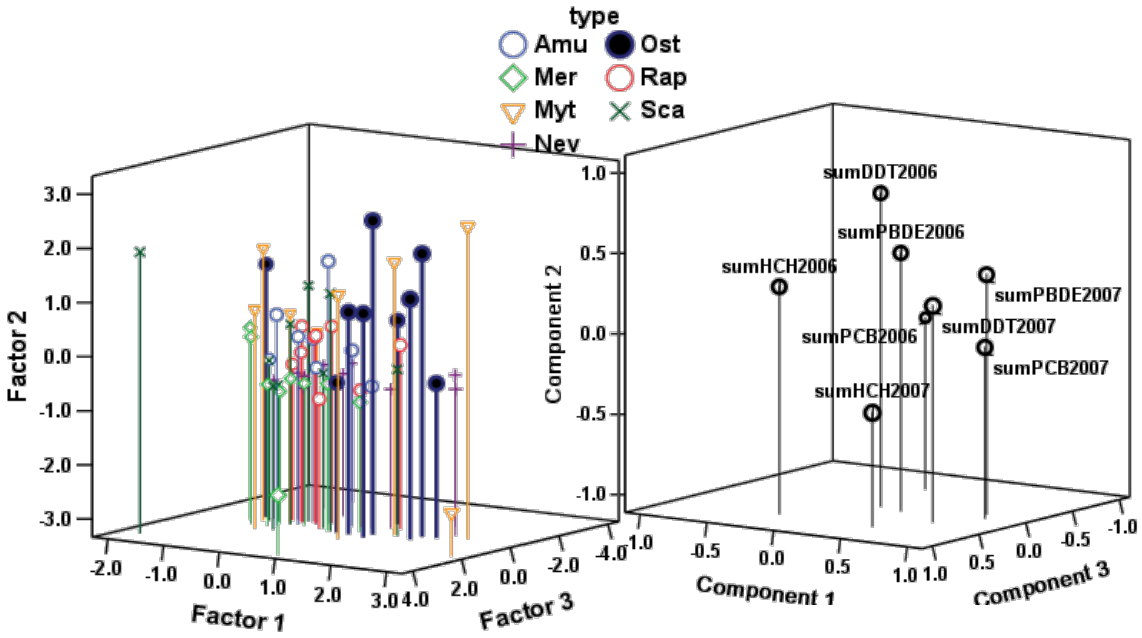

Figure 1 Loading and score plot from PCA using the database of total OCP, PCB, and PBDE concentrations in mollusks collected from the coastal water in the Chinese Bohai Sea in 2006 and 2007.