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# Effects of hydrodynamics on the distribution of trace persistent organic pollutants and macrobenthic communities in Bohai Bay

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ABSTRACT

In recent years, the rapid economic development along Bohai Bay, has brought out continuous increasing of the pollution loads in the Bohai Sea, especially by the large coastal reclamation project, Tianjin Binhai New Area. In the period of 2007–2009, we collected the sediments of the main rivers, estuaries, intertidal zone, and near-shore area of Bohai Bay, and Macrobenthos associated with the marine sediments to assess the influence of hydrodynamics in the coastal environment on the pattern of trace contaminants and the macrobenthic community. Based on data derived from these samples, the levels of polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) in sediments followed the order PAHs > OCPs > PCBs > PBDEs. The higher concentrations of PCBs, OCPs, PAHs and PBDEs were found in the estuarine and near-shore environment of the Dagu Drainage River. The spatial distribution of OCPs was different to that of PCBs due to the direction of the velocity field of Bohai Bay in its old and new topography, and the higher water-solubility of OCPs than that of PCBs. The results of the Pearson correlation and the PCA indicate that the medium diameter (MD) of sediments was the predominant factor influencing the distribution of PCBs and OCPs, most sampling sites were characterized mainly by TOC of sediments and biomass of macrobenthos. The results indicate that the distribution of trace contaminants and macrobenthic community in Bohai Bay are mainly affected by the hydrodynamic conditions.



## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs) are chemical substances that persist in the environment, bio-accumulate through the food web and pose a risk of causing adverse effects to human health and the environment. Their partitioning over the various biotic and abiotic compartments depends partly on their water solubilities, lipid materials and biological and hydrodynamic factors. These contaminants have been observed in sediments (Guzzella et al., 2005; Jin et al., 2008) and marine organisms (Ramu et al., 2007).

The environmental conditions in aquatic systems determine the accumulation and circulation of these contaminants. Physical and textural properties of the water column and marine sediments determine their interactions and the interactions between abiotic and biotic surfaces (Cornelissen et al., 1997). The fate and migration of non-polar organic contaminants depend on the particle size of sediments rather than the bulk sediment itself (Lee et al., 2006).

Macrobenthos are defined as invertebrates living in or on the sediments, they are good biotic indicators of environmental quality (Reice and Wohlenberg, 1993). The dynamics of macrobenthic assemblages are important in helping us to understand the ecological process of the inter-tidal ecosystem (Yuan and Lu, 2002). Bivalves, especially mussels, are widely used as sentinel organisms for monitoring chemical contaminants in coastal and estuarine ecosystems because they, being filter feeders, bioaccumulate contaminants. This approach has become popularly known as the "Mussel Watch Program" and has been adopted in many countries to study environmental contaminant levels (Monirith et al., 2003).

In recent years, the economy along Bohai Bay has developed rapidly, especially the Tianjin Lingang Industrial Area. Due to the continuous increase of the pollution loads and the poor capacity of the receiving water to self-clean, the research of ecological environment of Bohai Bay requires much attention. Other researchers have determined the levels of PAHs (Shi et al., 2005), OCPs (Yang et al., 2005), PCBs (Liu et al., 2007), and PBDEs (Wang et al., 2007) in sediments from the rivers of Bohai Bay, studied the hydrodynamic characteristic of Bohai Bay (Tao, 2006), and investigated the structure and diversity of macrobenthos communities of the Bohai Bay (Yang et al., 2005). However, no information on the

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effects of hydrodynamics on the distribution of trace persistent organic pollutants and macrobenthic communities in Bohai Bay is available yet. So, from 2007 to 2009, we collected the sediments of the main rivers, estuaries, intertidal zone, and near-shore area of Bohai Bay, and also collected macrobenthos associated with the marine sediments; the aims were: (1) to describe and analyze the effect of the hydrodynamics and the trace persistent organic pollutants on the structure and diversity of macrobenthic communities of the Bohai Bay; (2) to provide a study of the effect of the hydrodynamics on the transport of the trace persistent organic pollutants in Bohai Bay.

## 2. Materials and methods

### 2.1. Study areas and sampling strategy

#### 2.1.1. Bohai Bay

This is a shallow water basin with a very mild-slope beach and mostly fine mud bottom. The mean water depth of Bohai Bay is about 10 m, the width of tideland of Bohai Bay is 3–5 km and the average velocity of residual current is less than 0.1 m $s^{-1}$. The water exchange between Bohai Bay and Bohai Sea is weak, and the physical self-cleaning capacity of Bohai Bay is very poor (Tao, 2006). It has a dense network of rivers, and these water bodies receive both industrial and domestic wastewater discharge from Beijing, Tianjin and Hebei Province. All the wastewater entering the rivers and channels drains directly into the near-shore waters of the Bohai Bay. Its topography has been changing in recent years due to a large coastal reclamation project: the Tianjin Binhai New Area.

#### 2.1.2. Sediments

The main riverine, estuarine and intertidal zone sediments were collected at locations (sites R1–R6, E1, E3, I1, I2, a, f; Fig. S1 and Table S1 given in Supplementary material) along the Bohai Bay coastline, in May 2007. At least three sub-samples were collected for each sample type at each location. The sub-samples were then mixed thoroughly into a composite sample to reduce the possible random variation. The marine sediments were collected at locations (sites 1–22 excepting No. 4; Fig. S1) in near-shore area of the Bohai Bay in April 2008 on board the vessel Ludiyu 4548. The macrobenthic fauna associated with the marine sediments were also collected. Sediments from Dagu Drainage River, estuary and Haihe estuary were collected at sites b, c, d, e, E2 (Fig. S1) in April 2009. The sediments were collected with van Veen grab sampler. All samples were wrapped in acetone-cleaned aluminum foil, then sealed in plastic bags and stored in an ice box. The samples were frozen immediately on arrival at the laboratory and stored at −20 °C until analyzed.

#### 2.1.3. Macrobenthic community

The macrobenthos samples were collected using a modified 0.1 $m^2$ Gary-O'Hara box-corer. Triplicate sediment samples were brought on-deck, pooled and sieved onto 1 mm mesh. Retained organisms were preserved in 10% formalin. In the laboratory, organisms were counted under stereoscopic microscope and identified to species and family level (Kramer et al., 1994).

#### 2.1.4. Sample processing

The sediment granulometry was determined using a Mastersizer 2000 particle size analyzer (Malvern Instruments Ltd., Malvern, Worcestershire, UK) capable of analyzing particle sizes between 0.02 and 2000 mm. The percentages of each grain size group were determined, and the medium diameter (MD) of sediments and the grain size distribution curves were obtained.

### 2.2. Chemical analysis

#### 2.2.1. Total organic carbon

Analysis for total organic carbon (TOC) followed the method of Gaudette et al. (1974).

#### 2.2.2. Sample extraction and cleanup

PCBs and PBDEs were analyzed following USEPA 1668A and USEPA 1614. Briefly, the sediments samples were spiked with 1 ng of a $^{13}C_{12}$–PCBs mixture (EPA 68A–LCS mixture, Wellington Laboratories Inc., Ontario, Canada) and a $^{13}C_{12}$–PBDEs mixture (EO-5277, Cambridge Isotope Laboratories Inc., Andover, MA, US), respectively, mixed with anhydrous sodium sulfate and allowed to equilibrate for 12–24 h. The samples were extracted using *n*-hexane:acetone 50:50 (v/v) with ASE300 (DIONEX). The extracts were purified and fractionated following the detail description by Zhao et al. (2010).

OCPs and PAHs were extracted as follows: the samples were spiked with 4 ng of a 2,4,5,6-tetrachloro-m-xylene (TCMX, Supelco , Bellefonte, PA, USA) and $^{13}C_{12}$–PCB209 (Cambridge Isotope Laboratories Inc, Andover, MA, US) for OCPs, and a 2-flurobiphenyl (2-FBP) (Supelco, Bellefonte, PA, USA) for PAHs, then mixed with anhydrous sodium sulfate and allowed to equilibrate for 12–24 h. The samples were extracted using *n*-hexane:acetone 50:50 (v/v) with ASE300 (DIONEX).

The extracts were purified with deactivated silica (5%) columns for OCPs and with activated silica columns for PAHs, then the OCP fractions and the PAHs fractions were further purified with Gel Permeation Chromatography (GPC) columns, respectively; finally, the OCP fractions and the PAHs fractions were concentrated for injection into the analyzer, respectively.

#### 2.2.3. Instrumental analysis

PCBs and PBDEs were analyzed by isotope dilution high-resolution GC/MS using an Agilent 6890 gas chromatograph coupled to an Autospec Ultima mass spectrometer (Waters Micromass, Manchester, UK). The details are described by Zhao et al. (2010).

The PAHs and OCPs were analyzed by low-resolution GC/MS using an Agilent 7890 gas chromatograph coupled to an Agilent 5975C mass spectrometer (Agilent Technologies, Inc., CA, USA) using an electron impact ionization source (EI) in the selected ion monitoring (SIM) mode (the detail description given in Supplementary material).

#### 2.2.4. Quality control

Prior to analysis of the samples, the initial precision and recovery were carried with the bulk sediments from intertidal zone of Bohai Bay (the relative standard deviation (RSD) was lower than 12%). The method quality control was done by regular analysis of procedural blanks and ongoing precision and recovery (RSD < 20%) (the detail description given in Supplementary material).

## 3. Results

### 3.1. Bulk sediment geochemical parameters

Sediments from the intertidal zone of the west coast of the Bohai Bay are predominantly composed of silt and clay. The grain size of sediments from the near-shore of Bohai Bay consisted of silt with the MD range from 4.08 μm to 30.73 μm (site 2 was exceptional, Table S2). The probability distribution curve of sediment grain-size from sites 1, 2 and 9 showed two peaks indicating that these sediments were composed of many deposit sources or subject to many hydrodynamic forces.