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Baseline

Polychlorinated biphenyls and organochlorine pesticides in surface sediments from Shantou Bay, China: Sources, seasonal variations and inventories

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ABSTRACT

Sediments from Shantou Bay, China, were analyzed for polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) for the first time. The concentrations of PCBs and OCPs were 0.54–55.5 ng g^{-1} and 2.19–16.9 ng g^{-1} (dry weight), respectively. Source identification showed that tri-CBs and penta-CBs were manufactured and used in the last century, while usage of antifouling paint might still serve as a significant source of sediment DDT. Concentrations of PCBs and HCHs significantly ($p < 0.05$) increased after wet season, suggesting that atmospheric deposition and surface runoff played an important role in distribution of historical pollutants. Additionally, the adverse biological effects could occasionally occur for DDT in sediments. The mass inventories were preliminarily calculated for PCBs (90.1 ng cm^{-2} and 0.09 tons) and OCPs (61.8 ng cm^{-2} and 0.062 tons) in Shantou Bay, while as part of the "reservoir" of organochlorine compounds to the global ocean, its role cannot be neglected.

The pollutants carried by surface runoff entering the sea have a tremendous ecological and toxicological influence on the estuaries, coastal areas, and even continental shelf (Lin et al., 2016). Pollutants, especially persistent organic pollutants (POPs), are prone to accumulate in sediment. Estuarine and coastal sediments are reported both as sinks and secondary sources of POPs (Chen et al., 2006). Rivers contribute 95% of sediment from land to the ocean (Syvitski et al., 2005). Many studies focused on the estuaries of great rives, such as Pearl River, Yangtze River, Colorado River, etc. (Adeleye et al., 2016; Chen et al., 2006; Lugo-Ibarra et al., 2011). Presumably, due to the huge amounts of small estuaries, their role cannot be neglected in transportation of POPs to the global ocean.

Shantou Bay is an estuarine bay in South China, receiving freshwater inputs from Rong River and Mei River with average annual flow of 6.25×10^9 m^3 yr^{-1} (Luo et al., 1996). It consists of the upper bay and the lower bay, Niutian Bay (NTB) and Shantou Harbor (STH), respectively, covering an area of approximately 100 km^2 (Qiao et al., 2013). During May to August, monsoon brings heavy precipitation and significantly increases amount of surface runoff in Shantou Bay and its adjacent areas. It is characterized as developed fishery, a deep-water international harbor and a metropolis with 500 million populations (Shi et al., 2016). The rapid economic development and urbanization during the last 3 decades have resulted in serious environmental pollution in Shantou (Qiao et al., 2013). However, little is known about the environmental process of POPs in Shantou Bay.

POPs, such as PCBs and OCPs, have been a worldwide environmental concern due to their ubiquitous, persistence, long range transportation and toxic effects to living organisms (Combi et al., 2013; Nadal et al., 2015). Although Chinese government has banned the usage of PCBs, DDT and HCH for a long time, the huge amount of history usage can cause a duration effects to the environment (Lin et al., 2016). Worse yet, some studies reported that usage of DDT containing products still occurred in China (Lin et al., 2009; Yu et al., 2011a). To protect the health of human beings and ecosystems, monitoring the effects of PCBs and OCPs in some typical areas, especially some densely population area, has still been significant. Against this background, this study aimed to answer these questions: (1) how is the current situation and seasonal variations of POP contamination, (2) whether or not fresh input of POPs and (3) how much the POP contribution to global ocean from Shantou Bay based on the mass inventory concept.

Sediment samples were collected from 11 sites within NTB and STH in May and October 2011, respectively (Fig. 1). Based on the precipitation in Shantou Bay, the wet season is from May to September. Each sampling site represented each part of the study area, which indicated hydrodynamic and anthropogenic effects (e.g. N5 located Mei River Estuary and near a dockyard). More information about the sampling locations was detailed in Table S1 (Supplementary material). The top 5-cm sediment was taken using a stainless steel grab sampler and 3 subsamples were mixed well in situ in each sampling site. Each composite

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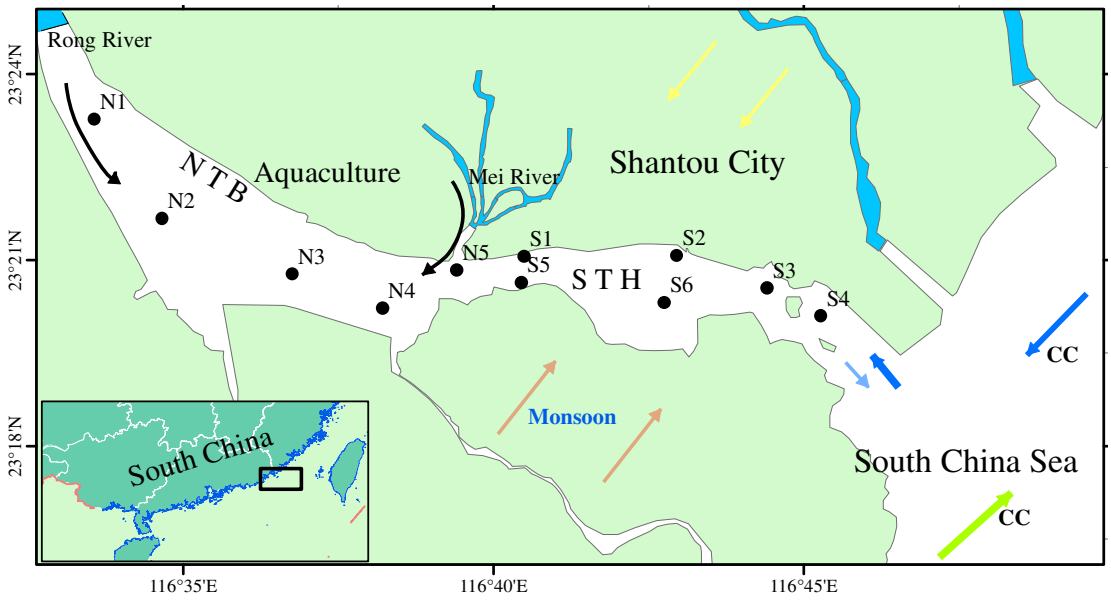

Fig. 1. Schematic of study area and sampling locations: Shantou Bay, China. CC: coastal current.

sample was wrapped into the pre-washed aluminum foil and sealed in a PE plastic bag. All samples were immediately kept in an icebox, transported to the laboratory and stored at −20 °C until analysis.

In the present study, the determination of OCPs and PCBs was carried out using the procedures modified from (Shi et al., 2013). Briefly, samples were freeze-dried, ground and passed through 100-mesh sieves. For each pulverized sample, 5.0 g was spiked with surrogate standards (PCB209) and soxhlet extracted with 150 ml mixture solvent (acetone: hexane: dichloromethane at 1:1:1) for 18 h. After extraction, activated copper powders were added to remove sulphur. The concentrated extract was purified using a chromatography column (5 g alumina and 8 g silica gel). The target fractions were obtained by 20 ml hexane/dichloromethane (1:1, v/v) and 15 ml of dichloromethane. Finally, the combined eluate was reduced to 200 μl under a soft stream of pure nitrogen for instrumental analysis.

The OCPs and PCBs were quantitatively analyzed by an Agilent Technologies 6890 N Network Gas Chromatography System with micro Electron Capture Detector (GC/μECD) and a DB-5 fused silica capillary column (30 m × 0.32 mm × 0.25 μm). The column oven temperature was programmed as follows: 110 °C for 2 min, increasing 10 °C per minute to 180 °C, followed by 5 °C per minute to final 280 °C, which was held for 20 min. Total run time was 49 min.

The sediment samples were analyzed for the following compounds: PCBs (including 26 congeners, known as IUPAC# 8, 18, 28, 29, 44, 50, 52, 66, 77, 87, 101, 104, 105, 118, 126, 128, 138, 153, 154, 170, 180, 187, 188, 195, 200 and 206), DDTs (*o,p′*-DDT, *p,p′*-DDT, *p,p′*-DDE and *p,p′*-DDD), HCHs (α-HCH, β-HCH, γ-HCH and δ-HCH), Chlordanes (CHLs, including heptachlor, heptachlor epoxide, oxy-chlordane, trans-chlordane and cis-chlordane), HCB, aldrin, dieldrin and endrin. The target compounds were quantified by the internal standards calibration.

Prior to quantification by GC-ECD, the OCPs and PCBs were identified on Agilent Technologies 6890 N Network Gas Chromatography System and Agilent Technologies 5973 inert Mass Selective Detector (GC/MS) EI with a DB-5MS fused silica capillary column (30 m × 0.32 mm × 0.25 μm). The temperature programming was the same as that just described in the GC-ECD. The mass spectrometer was operated in the electron impact/selected ion monitoring (EI/SIM) mode.

A Procedural blank, spiked blanks, duplicate samples and a Standard Reference Materials (SRM 1941, purchased from National Institute of Standards and Technology, USA) sample were analyzed along with field samples. The recoveries of PCB 209 in all samples were 82.5–109.7%, meeting the acceptable range established by USEPA. The results in spiking tests were 103 ± 9% for PCBs, 101 ± 6% for DDTs, 100 ± 12% for HCHs, 103 ± 5% for CHLs and 95 ± 4% for HCB, respectively, while measured concentrations of target compounds in SRM 1941 were within 85% to 110% of the certified values.

All of the reported concentrations were normalized on dry weight basis except where indicated. All the data were statistically analyzed using SPSS 17.0 and Origin 8.5. The map was plotted using ArcGIS 10.2 software.

The concentrations of ∑26PCBs in surface sediment samples were 0.54–26.9 ng g^{-1} (median: 2.66, mean: 5.25 ng g^{-1}) in May and 4.86–55.5 ng g^{-1} (median: 13.8, mean: 18.7 ng g^{-1}) in October, respectively. The levels of PCBs in October were significantly ($p < 0.05$) higher than those in May. Similar results about seasonal variations were reported in Liaohe River, China, Yangtze Estuary, China and North Sea, Belgium (Everaert et al., 2015; Gao et al., 2013; Lv et al., 2015). Geographically, the NTB had higher PCB level (15.3 ng g^{-1}) than that of STH (9.26 ng g^{-1}). The highest concentrations were found from N5 and N2 (NTB) in May and October, respectively; the lowest concentrations were found from S2 and S1 (STH) in May and October, respectively (Fig. 2); indicating that mobility and deposition of PCBs might be affected by regular dredging operations in shipping channels (Martins et al., 2012). Additionally, deposition of PCBs might be promoted by the effects of river runoff and tide in NTB due to its semi-closed and wide structure.

Some publications have reported PCB levels in surface sediments from other coastal regions around the world, while there is still no information reported in the Shantou Bay (Fung et al., 2005; Karacık et al., 2013; Pikkarainen, 2007; Richardson and Zheng, 1999). As shown in Table 1, compared to other coastal areas in China, the PCB levels in Shantou Bay were comparable to those in Yangtze Estuary, Haihe Estuary, Jiulong River Estuary and Hong Kong, evidently lower than in Pearl River Estuary and higher than in Beibu Gulf. Compared to other countries and regions, the levels in this study were comparable to those in Muroran Port (Japan) and Sarno Estuary (Italy), higher than those in coast of Korea, Red Sea (Egypt), Baltic Sea, Guaratuba Bay (Brazil) and Colorado River (Mexico), while much lower than those in Trinidad and Tobago, Istanbul Strait (Turkey) and Housto Harbor (USA) (Table 1).

The homolog profiles of PCBs are presented in Fig. 3. For individual PCB, PCB8, PCB18 and PCB29 were the three most abundant congeners,