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Distribution of organochlorine pesticides in sediments from Yangtze River Estuary and the adjacent East China Sea: Implication of transport, sources and trends

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HIGHLIGHTS

- OCP residues were at the low or comparable levels of the global range presently.
- Distribution of OCPs showed a "band type" pattern and controlled by ocean current.
- Distribution of OCPs also influenced by transmission media and redox conditions.
- Fresh sources and increasing contaminant trends of OCPs existed in the coastal area.
- OCPs in YRE and adjacent ECS are active sources of these chemicals to global sea.

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ABSTRACT

Thirty-eight surface sediments and two sediment cores were collected from Yangtze River Estuary (YRE) and adjacent East China Sea (ECS) to study the distribution patterns, origins, potential transport and burden of organochlorine pesticides (OCPs) in the marginal sea. Residues of OCPs ranged from 0.190 to 5.17 ng g^{-1} dry weight with a distinct "band type" pattern under the control of Yangtze River inputs and ECS circulation system. Differences in transmission media and redox conditions *in situ* respectively resulted in the divergent distributions of α/β-HCH and DDD/DDE. The compositional pattern analysis implied that OCPs in the inner shelf of ECS were derived from both "weathered" and fresh sources, whereas those in the outer shelf of ECS had undergone high metabolism. Concurrent with the land–sea migration, vertical profiles of sediment cores showed increasing trends or rebound since the 1990s, characteristic of two evident "jumps" of DDE + DDD/DDT and DDT/DDE ratios. Moreover, the primary distribution pattern founded for HCHs and the considerable mass inventories calculated (6.20 metric tones for OCPs) together suggested that the contaminated sediments in the studied area to be a potential source of OCPs to the global ocean.

1. Introduction

Organochlorine pesticides (OCPs) are typical persistent organic pollutants, which continue to attract considerable scientific and regulatory interests due to their historically high production volumes, persistence, bioaccumulation, and potential negative impacts on non-target organisms (Jones and de Voogt, 1999). OCPs can be transferred from pollution sources to marine ecosystems through many pathways including atmospheric transport and deposition, direct and indirect discharge, and riverine inputs. Because of their hydrophobic properties, OCPs tend to strongly partition to particulate matter and settle through the water column to the sediments, which act as their temporary or long-term sinks (Chen et al., 2002; Jönsson et al., 2003). On the other hand, resuspension process in estuarine and near-coastal environments may act as a source of OCPs to the overlying water column (Eggleton

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and Thomas, 2004). Therefore, sediments have been extensively used to assess the pollution of water bodies, due to the general importance of sediment phase in the fate and transport of contaminants.

The Yangtze River Delta (YRD), one of the most urbanized and industrialized regions in China, is located in eastern China, adjacent to the East China Sea (ECS). This area is also an important production base for foodstuff, and has a record of the highest pesticide application in the country (Li et al., 2001; Zhang et al., 2009), which have resulted in significant HCH and DDT pollution towards the environment compartments (Qiu et al., 2004; Zhou et al., 2006; Zhao et al., 2009; Zhang et al., 2011) and living beings (Nakata et al., 2005; Zhao et al., 2009) in this region. These contaminants from the YRD may also enter the ECS through surface runoff, creating long-term adverse effects on the coastal resources. Inputs of organochlorine compounds through rivers/estuaries have been known as the additional sources of these chemicals in the water areas. Yangtze River and Qiantang River are the two important rivers in the YRD, which annually carry about 239.3 and 16.5 metric tones of OCPs (Wu et al., 1999), respectively, flowing into the Yangtze River Estuary (YRE) and Qiangtang River Estuary (QRE), and eventually draining into the ECS of the western Pacific Ocean. Moreover, the ECS is downwind from the Chinese mainland and is therefore susceptible to the deposition of a large quantity of aerially transported particles and associated pollutants (Zhang et al., 1992). Overall, the ECS, especially the sea areas contiguous with the YRD is expected to be a receptor/sink of OCPs in the view of local surface runoff, riverine discharge, and deposition from atmospheric outflow of the Asian continent.

Studies about the OCP residues in the YRE and the ECS have confirmed the universal existence of these chemicals in air (Wu et al., 2010, 2011), water (Li et al., 2012), sediments (Chen et al., 2002; Liu et al., 2003, 2008; Yang et al., 2005, 2010, 2011; Hu et al., 2011), suspended particulate matters (Liu et al., 2008; Li et al., 2012), salt marsh plants (Liu et al., 2006a), sediment-dwelling animals (Nakata et al., 2005; Ma et al., 2008), and fishes (Nakata et al., 2005) in recent years. The historical surface sediment data further considered that the sediment residues of DDTs in 1990s have dropped to about one-tenth of those in 1980s, but there has been little sign of any declining trend for the results between 1990s and 2000s (Table S1). In the mean time, similar trends have also been observed for some marine animals catching from the ECS, with a striking example of DDT residues in seafoods purchased from local market of Shanghai, increasing from 2.3 ng g^{-1} dry weight (dw) in 1992 to 21 ng g^{-1} dw in 2000 (Nakata et al., 2005). These results suggest that significant sources of OCPs remain active around the YRE and ECS, and a further research is needed to study how these chemicals have been transported from sources to the epicontinental seas.

In this work, data are presented on hexachlorocyclohexanes (HCHs), dichlorodiphenytrichloroethanes (DDTs) and chlordanes (CHLs) in thirty-eight surface sediment samples and two sediment core samples collected from the YRE and its adjacent ECS in October 2008. The objectives are to examine the spatial and temporal distribution patterns of OCPs in marine sediments on a regional scale, to find out indications of historical records of riverine and airborne input of these chemicals in the study area, further to reveal the influencing factors related to the accumulation of OCPs in marine sediments, and to provide new information to understand OCPs potential sources, transport pathways and fate in the marine environment. Moreover, mass inventory of OCPs is going to calculate in order to assess the potential risks of sediments as a new source of contamination to the oceanic environment.

2. Materials and methods

Details of this section can be found in Supporting Information, and a brief description is given below.

2.1. Sample collection

Thirty-eight multi-cores and two gravity core (marked C3 and C6) along seven transects were collected in October 2008, of which 26 sites were located within the inner shelf region (I) and 14 within the open shelf region (II), as defined by circulation pattern, topography and grain size distribution (Fig. 1) (Zhu et al., 2011). The detailed latitude and longitude of the sampling sites are also shown in Table S2. Immediately upon collection, all cores were sectioned and subsampled onboard. For C3 core, subsamples were sectioned at a 2-cm interval, and C6, at a 1-cm interval to the depth of 10 cm and at a 2-cm interval thereafter. For the multi-core samples, only 0–5 surface sediments were collected. All the surficial and core samples were wrapped into the pre-washed aluminum foils and stored at −20 °C until further processing. Subsamples were analyzed for total organic carbon (TOC) and the sediment cores were dated.

2.2. Instrumental analysis, identification and quantification

Instrumental analysis was performed by a high-resolution gas chromatography coupled with ^{63}Ni electron capture detector (HRGC–ECD, Agilent, USA). A known quantity of pentachloronitrobenzene was added as an internal standard prior to GC analysis with dual columns. Retention times provided primary identification but concentrations had to agree between columns ($0.67 < C_1/C_2 < 1.33$) to be accepted as positive identification. Moreover, random samples with sufficient amount were injected into high-resolution gas chromatograph coupled with electron capture negative ion–low resolution mass spectrometer (HRGC/ECNI–

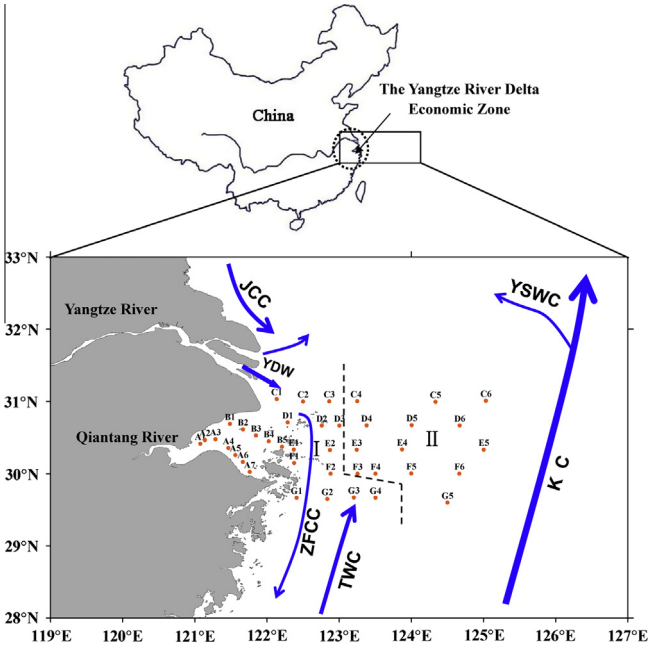

Fig. 1. Map showing sediment sampling stations in the Yangtze River Estuary and its adjacent East China Sea where decided into two box marked as: I, the inner shelf region; II, the open shelf region. The regional ocean circulation pattern in the East China Sea include YDW (Yangtze Diluted Water), JCC (Jiangsu Coastal Current), TWC (Taiwan Warm Current), YSWC (Yellow Sea Warm Current), ZFCC (Zhejiang Fujian Coastal Current), KC (Kuroshio Current).