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Spatial and seasonal distribution of organochlorine pesticides in the sediments of the Yangtze Estuary

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HIGHLIGHTS

- Spatial and seasonal variations of OCPs in four seasons are investigated.
- Changjiang diluted water impacts the deposition of OCPs in the inner estuary.
- Ocean currents play an important role on OCPs depositing in the offshore area.
- New sources of HCHs in the Yangtze Estuary or the upper stream are derived.
- The OCPs contents in the sediment core reveal the Three Gorges Dam's impact.

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ABSTRACT

The spatial and seasonal distribution of organochlorine pesticides (OCPs) in the sediments of the Yangtze Estuary was investigated. The total concentration of 19 OCPs ($\sum$OCPs), including α-HCH, β-HCH, γ-HCH, δ-HCH, *o*, *p*′-DDE, *p*, *p*′-DDE, *o*, *p*′-DDD, *p*, *p*′-DDD, *o*, *p*′-DDT, *p*, *p*′-DDT, heptachlor, aldrin, heptachlor epoxide (Isomer B, Isomer A), endosulfan I, dieldrin, endrin, endosulfan II and methoxychlor, in the surface sediments ranged from 0.4 to 82.1 ng g^{-1} d.w. The mean values of the $\sum$OCPs were 8.5 ± 8.3 ng g^{-1} d.w., 26.7 ± 12.1 ng g^{-1} d.w., 40.5 ± 18.2 ng g^{-1} d.w., and 13.0 ± 11.2 ng g^{-1} d.w. for August 2010, November 2010, February 2011 and May 2011, respectively. The highest concentration of OCPs was detected at the river–sea boundary because of the intense resuspension and redeposition of sediments in this area. The OCPs preferred to accumulate in the inner estuary, rather than in the offshore area in the dry season, whereas the opposite occurred in the flood season. This phenomenon was related to the seasonal changes of the Changjiang diluted water (CDW). OCPs in the offshore area were controlled by the ocean currents and the monsoon. There was a southward increase for the OCP deposition in the offshore area in the winter. This increase resulted from the influences of the southward Yellow Sea coastal current and the East China Sea coastal current, as well as the northwest wind in winter. The Three Gorges Dam had an impact on HCH composition by changing the sediment redistribution during the deposition process.

1. Introduction

Organochlorine pesticides (OCPs) comprise a series of persistent toxic chemicals and have been of considerable concern around the world due to their salient features of persistence, bioaccumulation, and toxicity (Willett et al., 1998; Wong et al., 2005; Yu et al., 2013). In 2001, nine OCPs, including aldrin, toxaphene, DDTs, chlordane, dieldrin, endrin, heptachlor, mirex, and hexachlorobenzene, were proposed to be controlled as persistent organic pollutants (POPs), a variety of organic chemicals that have lasting harms to environment and eco-systems. Due to their intensive utilization in agricultural and industrial activities, OCPs have been widely identified and reported across the world, even in the deserted plateau and the polar zone (Wania and Mackay, 1993; Blais et al., 1998; Cai et al., 2012). Moreover, a majority of these pesticides are endocrine-disrupting chemicals (Xue and Xu, 2006), which have been demonstrated to be among the most harmful substances to the endocrine system of human beings and wild animals. Because these chemicals pose great threats to the health of the ecosystem and human beings and have become one of the most prevalent environmental issues across the world, it would beis desirable and imperative to investigate their fates and transports in the natural environment, especially for countries with large-scale of OCPs adoptions.

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China experienced high production and consumption of OCPs in recent decades. Approximately, 4 and 0.27 million tons of technical hexachlorocyclohexanes (HCHs) and DDTs were produced over the years before the “opening and reform” in China, accounting for 33% and 20% of the total production around the world, respectively (Zhang et al., 2002). Although China has banned the production and sale of some types of high toxic OCPs since 1983, especially after signing The Rotterdam Convention in 2005, the environmental impact of OCPs is still worth attention (Meng et al., 2013).

The Yangtze River is one of the largest rivers in the world and is a main shipping route in China. The Yangtze River is flanked by agricultural reclamation areas. Therefore, OCP application during agricultural practice has a significant impact on the Yangtze basin environment. There are multiple studies on the survey and assessment of the OCP distributions and risks along the different reaches and catchments of the Yangtze River (Shu and Li, 2009; Yang et al., 2009; Wen et al., 2010; He et al., 2011; Tang et al., 2012). The run-off and the waste water of the whole basin finally arrive in the Yangtze Estuary. Thus, the water and sediment containing OCPs from the upper stream run-off results in OCP contamination at the estuary along with the local input from the Yangtze Delta. There are a few reports on the OCP contamination in the Yangtze Delta as well (Zhang et al., 2009; Liu et al., 2011; Shi et al., 2013), but rarely about the survey of OCPs in the Yangtze Estuary.

Recently, the sediment discharges of the Yangtze River have dramatically decreased due to the construction of dams, especially the Three Gorges Dam. As a result, the distribution of OCPs in the estuary could have changed because of its high adsorption on the sediment. However, there is no systematic study of the OCP distribution in the Yangtze Estuary. Recently, we collected a total of four seasons of surface sediment samples at the Yangtze Estuary and the offshore area in August and November 2010 and February and May 2011. Additionally, a sediment core was collected in May 2011. The surface sediments were expected to exhibit various influences on the spatial and seasonal distribution of OCPs. The sediment core elucidated the long-term trends of the OCP occurrence and deposition in the past decades. This study aimed to determine the spatial and seasonal distributions of OCPs in sediments and to analyze the impact factors of OCP deposition in the Yangtze Estuary.

2. Materials and methods

2.1. Study area and sampling

The 30 sampling sites are shown in Fig. 1. The sites covered the inner Yangtze Estuary and offshore. For a better understanding of the special distribution of OCPs, we divided the study area into three parts (Table 1). The North Branch contained only one site (No. 17) because the South Branch receives the most runoff from the Yangtze River (>95%), whereas the North Branch accounts for only 5%.

The surface sediment samples in the inner estuary and offshore where the sedimentation rate of suspended solids in this area was around 4 cm per year recently, were collected within the depth of 2–5 cm during August 2010, November 2010, February 2011 and May 2011. A sediment core was collected at N31°09.16710′ E122°26.33315′ (Fig. 1), near the −10 m isobath on May 2011 with a stainless steel static gravity corer (i.d. 8 cm). The core was divided into 3 cm intervals immediately after collection using a stainless steel blade. All the sediment samples (including surface and core sediment) were ground, homogenized, and stored at −20 °C until the analysis.

2.2. Chemicals

A standard mixture of 19 OCPs (α-HCH, β-HCH, γ-HCH, δ-HCH, *o, p*′-DDE, *p, p*′-DDE, *o, p*′-DDD, *p, p*′-DDD, *o, p*′-DDT, *p, p*′-DDT, heptachlor, aldrin, heptachlor epoxide (Isomer B), heptachlor epoxide (Isomer A), endosulfan I, dieldrin, endrin, endosulfan II, methoxychlor, OCP Solution Mix, 10 μg mL^{-1} in hexane) was used in the analysis. All the single OCP reference materials were supplied by the National Research Center for Certified Reference Material. All solvents used for sample processing and analysis (dichloromethane, acetone, hexane, and methanol) were chromatographically pure from J.T. Baker, USA. Deionized water was produced by a Milli-Q system (Millipore Co., USA). Anhydrous sodium sulfate and silica gel (100–200 mesh) were of analytical grade and were activated for 4 h at 450 °C to remove impurities.

2.3. Dating of the sediment core

The sediment cores were dated with ^{210}Pb and ^{137}Cs analysis at the Institute of Geography and Marine Science, Nanjing University (Flynn, 1968). The cores were stored for 3 weeks in sealed containers to allow radioactive equilibration. A 576AAlpha Spectrometer (EG&G, USA) was used. And IAEA2327 standard sample was used for the calibration.

2.4. Sample analysis

All the sediment samples were freeze-dried at −15 °C for 48 h until constant weights were maintained. The method of extraction of the sediment samples was the same as the extraction from sediments presented by Yang et al. (2005b). Quantitative analysis of the OCPs was conducted with an Agilent Technologies 7890A gas chromatograph equipped with a ^{63}Ni electron capture detector and a 30 m × 0.25 mm × 0.25 μm DB-5 capillary column (J&W, USA). The initial oven temperature was set to 80 °C; it was gradually increased to 190 °C at a rate of 20 °C min^{-1}. This temperature was maintained for 1.0 min and was then raised to 235 °C at a rate of 4 °C min^{-1} and held for 10 min. The temperatures of the injector and detector were maintained at 250 °C and 330 °C, respectively. Nitrogen was used as the carrier gas at a constant flow of 1.0 mL min^{-1}.

2.5. Determination of the particle size and total organic matter in the sediment

Ten grams of air-dried sediment were used to determine the content of total organic matter (TOM) by mass losses on ignition in a muffle furnace at 550 °C for 5 h. A particle size analyzer (Microtrac S3500, USA) was used to measure the particle size (PS) of the sediment sample. This analyzer uses three precisely placed red laser diodes (a patented tri-laser system) to provide an accurate, reliable and repeatable method to characterize particle size. This equipment was also used to analyze the particle size distribution of 15 groups of copper mine tailings. In brief, approximately 0.1 g air-dried sediment and 3 mL of deionized water were added to a glass test tube, which was then stirred by a vortex mixer for 10 min until the mixture was homogenized. A few drops (3–4) of the mixture were added into the mixing chamber of the sample delivery controller. The particle size distribution curve and the percentage of each fraction (defined as sand, silt and clay) of the sample were analyzed by the optical sensor automatically.

2.6. Analytical quality controls

Quantification was performed with the analytical duplicates, the method blank, and the external standard method using the