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Pollution levels of DDTs and their spatiotemporal trend from sediment records in the Southern Yellow Sea, China

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ABSTRACT

In order to study the pollution levels and spatiotemporal trend of Dichlorodiphenyltrichloroethanes (DDTs) in the Southern Yellow Sea (SYS), thirty-two surface sediment samples and a sediment core have been analyzed, and our results have been compared with previous reports. DDTs contents in our samples ranged from below detection limit to 5.1 ng/g dry weight (d.w.), which presented lower ecological risks in the SYS. Surface sediment results show a seaward increasing trend with high values in the northern region of the central basin of the SYS. Our reconstructed core record and historical data from previous reports reveal an increasing trend from 1905 to 1955 but a decline trend since 1985 for DDTs, which is consistent of the production, usage and banning of DDTs in China. The source identification, based on (DDE + DDD) / DDTs, suggested that aged DDTs were the major contributor, though there were some inputs of fresh DDTs from the usage of 1,1-bis(*p*-Chlorophenyl)-2,2,2-trichloroethanol (dicofol).

1. Introduction

Dichlorodiphenyltrichloroethanes (DDTs), as a class of semi-volatile persistent organic pollutants (POPs), have been designated as major pollutants of global concern for decades because of their environmental persistence, bioaccumulation, and ecological risks to plants, animals and human (Aigner et al., 1998; Lin et al., 2012b). In China, DDTs were widely used in agriculture as well as in malaria control, and the total production reached 270,000 t from 1960 to 1980 (Qiu et al., 2005). As a result, large amounts of DDTs were exposed to the environment. Due to their serious threats to ecosystems and human health, industrial production of DDTs was banned thereafter in 1983 and the outputs of DDTs declined (Zhang et al., 1999; Li et al., 2015). However, it has been indicated that some fresh DDTs still have been discharged into the environment as a result of export demand and dicofol production (Zhou et al., 2006; Li et al., 2015). As a synthetic compound with a high impurity of DDTs, dicofol, 2,2,2-trichloro-1,1-bis(4-chlorophenyl) ethanol, is extensively used for controlling mites, but it is harmful to cotton, fruit trees and vegetables. During dicofol production and usage processes, a high proportion of DDTs has been leaked into the environment (Qiu et al., 2005; Da et al., 2014).

Since organic contaminants in marine sediments can be accumulated over seasonal to decadal timescales, oceans often act as remote monitoring sites of regional distribution and temporal trend of POPs changes (Zhang et al., 1999; Wurl et al., 2006; Zhang et al., 2007; Lohmann et al., 2009; Lin et al., 2012b). The Yellow Sea (YS), one of the China marginal seas, is surrounded by China mainland on the west and the Korean Peninsula on the east (Zhang et al., 2008). Although the Yellow River and Yangtze River do not directly discharge into the YS, large amounts of terrestrial materials from these two rivers have been deposited in the YS due to transports by ocean currents (Huh and Su, 1999; Lim et al., 2007). In addition, the coastal areas of the southern YS (SYS) are densely populated, and aquaculture is highly developed (Yin et al., 2015). As a result approximately 7.6% of contaminants from municipal and industrial activities around the SYS coastal regions have been discharged into the SYS (China's State Oceanic Administration (CSOA), 2007; Ministry of Environmental Protection of the People's Republic of China (MEPPRC), 2007; Duan et al., 2013). Therein, marine sediments from the SYS have been used to determine POPs pollution levels and to evaluate their ecological risks (Shi et al., 2011; Da et al., 2013; Chen et al., 2014).

The contents and distributions of DDTs and their metabolites were

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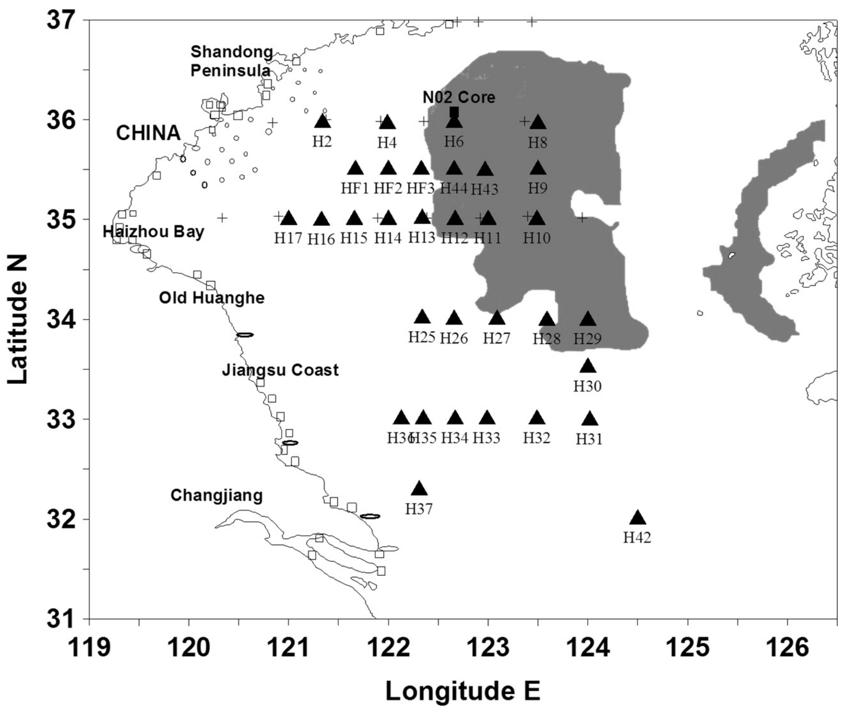

Fig. 1. Sampling sites in our study (marked by ▲ and ■) and previous studies in the SYS.
(a) ■: box sediment core (our study); (b) ▲: surface sediment in the central of the SYS collected in 2012 (our study); (c) +: surface sediment in the central of the SYS collected in 2007 (Hu et al., 2011); (d) ⬭: surface sediment in the coastal area of the SYS collected in 1991 (Ma et al., 2001); (e) □: surface sediment in the coastal area of the SYS collected in 1999 (Liu et al., 2008b); (f) ○: surface sediment in the coastal area of the SYS collected in 2007 (Wang et al., 2010). Mud areas are marked in gray.

often the focus in the early studies in the SYS. It has been noted that they were all presented at lower levels in the SYS, and the effects of human activities in the coastal areas were much greater than in the central SYS basin (Ma et al., 2001). For example, the contents of DDTs in the sediments collected in 2000 from the eastern part of the YS mud area ranged from 0 to 1.29 ng/g d.w. (Oh et al., 2005). While DDTs were at higher levels (average 7.72 ± 10.88 ng/g d.w.) in most sites in Haizhou Bay (Fig. 1) littoral regions of Jiangsu Province. Only one site the level exceeded the guideline for effect range median (ERM) (Long et al., 1998), with surface DDT content up to 62.9 ng/g d.w. (Liu et al., 2008b). Recently, the major source of DDTs was switched from industrial production into the usage of dicofol after the ban of industrial DDTs (Qiu et al., 2005; Liu et al., 2008b). Though the above limited data have indicated lower ecological risks of DDTs in the SYS, but their current and future risks are still uncertain possibly as a result of the resuspension from sediments caused by cyclonic eddy (Alexander et al., 1991; Bi et al., 2011; Hu et al., 2013), as well as from new inputs (Wong et al., 2005; Yin et al., 2015).

Previous studies have focused on the coastal areas of the SYS spatially, and few sediment records of DDTs were obtained to evaluate the temporal trend. In this study, thirty-two surface sediment samples and a sediment core from the central SYS have been collected for studying pollution levels, spatiotemporal trend and sources of DDTs, especially for the basin areas. Historical data of DDTs in both the coastal and the central SYS have also been compared here to evaluate their ecological risks.

2. Materials and methods

2.1. Chemicals used in the study

Isotope labeled compounds [$^{13}C_{12}$] o,p′-DDE, [$^{13}C_{12}$] p,p′-DDE, [$^{13}C_{12}$] o,p′-DDD, [$^{13}C_{12}$] p,p′-DDD, [$^{13}C_{12}$] o,p′-DDT and [$^{13}C_{12}$] p,p′-DDT (0.5 mg/L) were purchased from Wellington Laboratories, Inc., Canada. Pentachloronitrobenzene (PCNB) was acquired from Cerilliant, Cambridge Isotope Laboratories (Tewksbury, MA), and organochlorine pesticide standard mixture (US-1128), decachlorobiphenyl (PCB 209) and 2,4,5,6-tetrachloro-*m*-xylene (TC*m*X) were acquired from Ultra Scientific USA. HPLC grade hexane and dichloromethane as well as Na_2SO_4 were purchased from Sigma-Aldrich.

2.2. Collection of samples

The YS joins the Bohai Sea in the north and the East China Sea (ECS) in the south. It is separated into the SYS and the Northern Yellow Sea (NYS) by the Shandong Peninsula (Fig. 1). The Yellow River and Yangtze River provide substantial sediment inputs into the SYS, although both do not discharge directly into the SYS (Huh and Su, 1999; Lim et al., 2007). Short sediment cores from thirty-two sites were collected from the coast to the central basin of the SYS during a cruise in April 2012 (Fig. 1), using a stainless steel box-corer onboard the R/V Dong Fang Hong 2 of the Ocean University of China, Qingdao, China. Surface sediments (0–3 cm) from these sites were used for this study. Core N02 (122.634 °E, 36.050 °N, water depth of 64 m) was collected in the mud area of the SYS with a box corer during the cruise in 2011. The core was sectioned at 1 cm intervals to the depth of 33 cm for reconstructing DDT record. All samples were freeze-dried, homogenized, sieved through a stainless steel 75-mesh (0.5 mm) sieve and stored at − 20 °C until analysis.

2.3. Extraction and cleanup

Sediment samples (10 g) were spiked with surrogates of 50 ng TC*m*X and PCB209, then suspended with 3 g anhydrous Na_2SO_4 and ultrasonically extracted with 80 mL hexane/dichloromethane (v/v = 1:1) solution for 40 min and further kept overnight before collecting the extract. Then the sample was extracted again with 80 mL hexane/dichloromethane (v/v = 1:1) solution for another 30 min and with 20 mL hexane for 20 min respectively. Activated copper powder was used for desulphurization. All the extracts were rotary-evaporated to about 1–2 mL and further cleaned with a multilayer composite column consisted of activated silica gel (3 g), acid silica gel (6 g), activated silica gel (1 g) and anhydrous Na_2SO_4 (3 g) from bottom to top. The column was pre-cleaned with 60 mL dichloromethane/hexane (1:5, v/v) before loading each sample and then the extract was eluted in sequence with 30 mL of hexane and 30 mL of dichloromethane/hexane (1:9, v/v). The eluate was concentrated with a rotary-evaporator and then concentrated to 0.2 mL under gentle N_2 flow. The internal standard PCNB