Status of POPs accumulation in the Yellow River Delta: From distribution to risk assessment

Jing Li ^{1,2} Chunli Chen ^{2*} Fadong Li ^{1*}

1 Key Laboratory of Ecosystem Network Observation and Modeling, Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing 100101, China

2 Key Laboratory of Poyang Lake Environment and Resource Utilization of MOE; School of Environmental and Chemical Engineering, Nanchang University; Nanchang 330047, China

*** Joint corresponding authors:**

Chunli Chen, Key Laboratory of Poyang Lake Environment and Resource Utilization, Ministry of Education; School of Environmental and Chemical Engineering, Nanchang University; Nanchang 330047, China. E-mail: hncichen@163.com

Fadong Li, Key Laboratory of Ecosystem Network Observation and Modeling, Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing 100101, China. Phone: 86-10-64889530; E-mail: lifadong@igsnr.ac.cn

Abstract

The Yellow River Delta (YRD) is a large region of China with complex pollution sources and a long history of environmental deterioration. Despite this, relatively little data exists on the status of important contaminants of concern in this region. Here, we review the literature on the status of key persistent organic pollutants (POPs) of concern including organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs) in the YRD. Sources, source identification methods, and spatial distribution patterns are presented. Additionally, POPs contamination levels reported in the literature were evaluated against popular regulatory limits worldwide to form a basis for overall environmental health. Our review determined that OCPs in the YRD originated mainly from current pesticide use and past agricultural pesticide application. Sources of PAHs included petrochemical inputs, coal fired plants, and wood combustion. PCB levels were impacted by the petrochemical industry as well as waste disposal of PCB containing equipment. OCPs exhibited a spatial distribution pattern that increased along the urban-rural gradient, while the opposite was seen for PAHs and PCBs. Comparisons of POPs contamination levels in the YRD with popular regulatory limits suggest that the extent of PCB contamination all mediums (sediment, soil, water, and biota) exceeded that of PAHs and OCPs. Overall pollution levels in the YRD seem to be in control; however, levels from heavily polluted point sources raise numerous concerns about the ecological health of the region and require more attention from regulatory authorities.

Keyword

POPs; Environmental occurrence; Risk assessment; Origins; Yellow River estuary; Oil field

The Yellow River Delta (YRD) is a typical ecotone of the Yellow River and Bohai Bay (Xie *et al.* 2012) suffering from enormous environmental deterioration from industrialization. With an area of 2200 km², the watershed of the YRD is the largest and youngest wetland in the warm temperate zone of China (Yuan *et al.* 2012), and is also the youngest land in the world. Extremely high sediment loads (>1000 million tons per year, Mt/yr) have been discharged to the sea over thousands of years as a result of poor agricultural practices in the Loess region (Oliva *et al.* 2015). High sediment loading from the river and transport by hyperpycnal flows into the estuary have made considerable contributions to the deltaic depositional system (Fan *et al.* 2009). In the environment, persistent organic pollutants (POPs) tend to adsorb to organic matter due to their chemical properties. Once they enter aquatic environments, they preferentially sorb to organic particles and are deposited in sediments. Thus, large quantities of organic pollutants enter the Yellow river through this sediment loading (Yang *et al.* 2009). In China, dichlorodiphenyltrichloroethane (DDT) and hexachlorocyclohexane (HCH) were the most widely used and produced organochlorine pesticides (OCPs). These OCPs were produced for use in agriculture, forestry, and public health for more than four decades (Cai *et al.* 2008).

Due to their bioaccumulation potential, persistence, toxicity and long-range environmental transport ability, POPs are of great concern to scientists, environmental quality managers and policy makers (IPCS 2000; Keita-Ouane *et al.* 2001; UNEP 2003; Peterson *et al.* 2010). Measurement of their concentrations and evaluation of ecological risk in a large-scale region is of significant importance to protect environmental health (Sudaryanto *et al.* 2011). A large amount of work has been carried out regarding state of POPs globally. The United Nations Environment Programme (UNEP) (UNEP 2003), International Programme on Chemical Safety (IPCS) (IPCS 2000), Intergovernmental Forum on Chemical Safety (IFCS) (Peterson *et al.* 2010), Inter-Organization Programme for the Sound Management of Chemicals (IOMC) (Keita-Ouane *et al.* 2001) and other international organizations are actively involved in the research of characteristics, hazards, fate, etc. of POPs.

With the rapid economic development in China over the last few decades, environmental pollution caused by POPs has been identified in several delta areas, e.g., the Mekong Delta (Cenci and Martin 2004), the Pearl River Delta (Yang *et al.* 2007), and the Yangtze River Delta (Yang *et al.* 2009). Most investigations of pollutants in the YRD have focused on three main POPs of

concern: OCPs, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) (Fan *et al.* 2009; Hu *et al.* 2010; Liu *et al.* 2010). It is important to note that the Shengli Oil Field, the second largest oilfield in China, is located in the YRD. Given the scale of mining and oil refining activities occurring here, it is of significance to assess the ecological risk of petroleum contaminants in this area. A comprehensive investigation of the distributions of POPs in the YRD will be useful to determine the sources, evaluate ecological risks, and create remediation strategies.

This review is organized as follows: Firstly, previous usage of POPs and potential pollution sources in the YRD are described. Secondly, environment occurrence is introduced on a matrix-specific basis, i.e., soil, sediment, water, and organisms. Thirdly, environmental sources are identified mainly focusing on historical agriculture usage, technical production, atmospheric deposition, and riverine transport. Finally, potential environmental effects are examined through comparisons between environmental quality guidelines and levels of POPs in environmental matrices.

Fig.1 The location of YRD and the shifting history of the Yellow River

The YRD is a rapidly developing petrochemical and agricultural area of China with a long history of pollution and complex sources of contamination (Fig. 1). From 1960 to 1990, large amounts of lindane, dicofol, and technical DDT in China were produced as well as widely used for pest control. It has been estimated that approximately 258, 000 tons of HCH and DDT were used in China in 1990, accounting for 74.0% of all pesticide use (Tao *et al.* 2007). Agricultural usage of HCHs and DDTs lasted from 1953 to 1993 in the YRD (Tao *et al.* 2006).

PAH contamination is derived from petroleum sources (i.e., petrogenic sources) and from incomplete combustion of carbonaceous materials (i.e., pyrogenic sources). These sources occur naturally and as a result of human activities (Edwards 1983). Cracking and refining of petroleum and incomplete combustion of fossil fuels are known to produce large amounts of PAHs (Xie *et al.* 2012). **Crude oil cracking sites**, oil wells, and petrochemical industrial activities are point sources of PAHs, which can increase regional levels of PAH contamination through short-range and long-range transport (Wilcke 2007). The Shengli Oilfield is **arguably the largest point source** of PAH contamination in the YRD. **Oil well** blowouts, leaks and spills from underground tanks, pipelines and illegal disposal **threaten the ecosystem in this area**. Manufacturers in the YRD have **by-produced PAHs** (Hu *et al.* 2005). Effluents from several production facilities were treated ineffectively and wastewater discharged from these **facilities** contributed large amounts of PAH contamination (Li *et al.* 2006). Sewage irrigation was used at a very large scale in this area for over 30 years because of the shortage of water resources (Gong *et al.* 2004).

PCBs have a long history of extensive production and use in China. It has been estimated that 10,000 tons of **PCB 3 (9000 t) and PCB 5 (1000 t)** were produced **in China** from 1965 to 1974 (Xing *et al.* 2005). PCB 3 was used primarily in power capacitors applied in electricity production, distribution and transmission, **and** PCB 5 was used mainly as a paint additive in China (China SEPA 2003). Furthermore, following the ban on the production and use of PCBs, most of the outdated PCB-containing equipment (equipment filled with PCBs as dielectric fluid) was removed from use and stored. Potential POPs pollution sources at YRD are listed in Table 1.

Table 1 Previous usage of POPs and potential pollution sources in the study area ^a

Pollutants(group)	Potential emission/pollution sources/Usage in China	Potential emission sources in the YRD
HCH: Technical HCH and Lindane	Mainly used in agriculture, pest control in rice, wheat, soybean, maize, cotton, sorghum and orchard; a small apportion was also used in forestry and public health;	Extensive application in agriculture and forestry; Wastewater irrigation; Major use on wheat land
DDT and its metabolites: Technical DDT	Disease vector; intermediate of dicofol production; antifouling paint for ships; Export for controlling malaria; Insecticide in orchards, paddy fields and	Extensive application in agriculture and forestry; Transportation leakage; Wastewater irrigation; Waste product dumps;

	vegetable fields(until 1983); mosquito-repellent incense(until 2002) ; Acaricide in agriculture (apple, orange and cotton)	
Dicofol (10%DDT impurities)		Dicofol application on cotton;
PCB	10,000 tons of PCBs were produced from 1965 to 1974; Power capacitors; Paint additive; Heat exchangers; Hydraulic systems, Carbonless copy paper; Industrial oils; Additives; Flame retardants and other	Power capacitors; Paint additive; Water runoff (non- point source) from the industrial production and use by the enterprises along the Yellow River; PCB waste storage; Oilfield drilling activities;
PAH	Petroleum sources (i.e., petrogenic sources) and from incomplete combustion of carbonaceous materials (i.e., pyrogenic sources)	By-product of crude oil, oil wells, and petrochemical industrial activities; Oil well blowouts, leaks and spills from underground tanks; Pipelines and illegal disposal; Manufacturers; Sewage irrigation;

^a Sources: (China SEPA 2003; Gong *et al.* 2004; Hu *et al.* 2005; Li *et al.* 2006; Tao *et al.* 2006; Tao *et al.* 2007; Wilcke 2007; Wang *et al.* 2009).

Soil **is** the largest sink in the environment and significantly influences **human and environmental health**. In China, OCPs, PAHs and PCBs were the most frequently studied POPs in soil (Xing *et al.* 2005), and concentrations of POPs in soil have been increasing for 100-150 years, especially in urban areas (Cai *et al.* 2008). In the YRD, more than 400 soil samples collected from different cities and regions have been analyzed for the occurrence of OCPs, PAHs and PCBs.

Soil OCPs have been investigated in **at least 10** studies. DDTs (*p*, *p'*- DDT, *o*, *p'*- DDT, *p*, *p'*- DDE, *o*, *p'*- DDE, *p*, *p'*- DDD, *o*, *p'*- DDD) and HCHs (α - HCH, β - HCH, γ - HCH, δ - HCH) were the main contributors. **Occurrences of OCPs in soil in** various parts of YRD **are** described in Table 2 (all concentrations are normalized to dry sample weight). Concentrations of DDTs ranged from 0.05-3819 ng/g (Fig. 2). **Spatial** distribution varied greatly and rendered a clear upward trend along the urban-rural gradient (Chen *et al.* 2011; Xie *et al.* 2012). **DDT concentrations** in rural areas varied between 4.10-3818.76 ng/g (with a mean of 315.65 ng/g), whilst that in the city varied from 3.34-533.53 ng/g (with a mean of 63.81 ng/g) (Chen *et al.* 2011; Yuan *et al.* 2011). Among DDTs, the predominant compound was *p,p'*-DDE, which accounted for 63.0% - 82.7% of the DDT concentration, followed by *p,p'*-DDT, and **lastly** was *p,p'*-DDD.

The distribution pattern of DDTs varied among urban, suburban, and rural areas. Along an urban-rural gradient, the *o,p'*-DDTs (*o,p'*-DDT, *o,p'*-DDE, and *o,p'*-DDD) percentages declined significantly, from 38.3% to 4.3% (Xie *et al.* 2012). One possible explanation is that after the ban of DDT for agricultural production, chemicals containing *o,p'*-DDT, such as dicofol, contributed more to DDT pollution in urban and suburban areas than in rural areas.

The Yellow River was artificially diverted from the Old Course to the Modern Course in 1976 (Fig. 1). After the Yellow River diversion, more than 450 km² new land was made in the Yellow River estuary with the sediment deposition speed of 13 km²/year. At the same time, a series of ecological problems occurred in the Old Course of the Yellow River, including the shrinkage of wetlands, deterioration of water quality, water and soil erosion, and decreased agricultural activities. The area between the Old Course and the Modern Course built up the Middle Area. Concentrations of soil OCPs in Modern Course, Middle Area and the Old Course of the Yellow River were 1.4-39.9, 2.9-22.7, 3.7-36.1 ng/g (Zhang 2011). A comparison of DDTs concentrations among the Modern Course, Middle Area and the Old Course of the Yellow River was in the order of Old Course > Modern Course > Middle Area, with the mean values were 3.28, 1.23 and 1.15 ng/g, respectively (Zhang 2011). Concentrations of HCHs ranged from 0.01-18.5 ng/g (with a mean of 3.34 ng/g), and showed the trend of Modern Course > Old Course > Middle Area. Due to its low volatility, high stability and poor biodegradability, β -HCH was the most stable isomer of HCH residues, accounting for 46% of the total HCH content. Other HCH isomers showed the trend of β -HCH > δ -HCH > α -HCH > γ -HCH in most measured soils (Zhang 2011).

Fig.2 The spatial distribution of soil POPs in the YRD

(Data are from references of Tao, 2008; Fan *et al.*, 2009; Liu *et al.*, 2010; Chen *et al.*, 2011; Zhang, 2011; Xie *et al.*, 2012a; Xie *et al.*, 2012b; Yuan *et al.*, 2012; Da *et al.*, 2014)

PCBs generally enter the air, soil, water and sediment during their manufacture and use (Wong and Poon, 2003). Few studies have surveyed PCB contamination in soil, and when undertaken, the focus was on already heavily polluted areas in China (Xing *et al.* 2005). Measured soil concentrations of PCBs in the YRD ranged from non-detectable to 124.2 ng/g and were dominated by heavily chlorinated PCBs (PCB-101 and PCB-118) (Zhang 2011). Soil PCBs concentrations were significantly greater in urban than suburban or rural areas (Xie *et al.* 2012). The mean concentration of PCBs in the urban area was 6.3 ng/g, whilst that in the suburban and rural area was 1.9 ng/g and 1.6 ng/g, respectively. The production of PCBs was stopped in 1980s in China, four years after Yellow River was diverted into the two courses. The spatial pattern of soil PCBs showed the trend of Old Course > Modern Course > Middle Area. Concentrations ranged from 15.6-124.2 ng/g, 9.3-65.4 ng/g and 19.0-73.8 ng/g, with mean value of 45.0, 35.7 and 29.5 ng/g, respectively (Zhang 2011). In general, low-chlorinated PCBs (such as PCB 28 and PCB 52) were more concentrated in the Modern Course while heavily chlorinated PCBs such as PCB 180 and PCB 138, among others, were more concentrated in the Old Course.

Concentrations of 16 PAHs listed for priority control by the USEPA have been measured in soil in the YRD. Concentrations varied over the range of 25.5 to 2176.0 ng/g, with an average concentration of 229.8 ng/g. Concentrations significantly increased along the rural-urban gradient

($P < 0.05$) (Tao 2008; Xie *et al.* 2012). Average PAH concentrations in the rural and suburban areas were 278.7 ng/g and 284.6 ng/g, respectively, far exceeding naturally occurring background levels of a typical indigenous soil that result from plant synthesis and natural fires (Tao 2008). PAHs are compounds composed of one or more benzene rings with varying degrees of persistence, toxicity, and mutagenicity based on molecular weight of the compound. Environmentally significant PAHs are those with two to seven benzene rings. Low molecular weight PAHs (2-4 rings) tend to be more acutely toxic, while high molecular weight are not, (though have other deleterious effects). The relative proportion of two to six ringed PAHs in the YRD ranged from 6.75% to 40.84%. Four-ring PAHs made up the largest relative proportion of soil PAHs and two-ring PAH made up the smallest proportion. Generally speaking, PAHs with more rings accounted for a dominant proportion of soil PAHs (Cao *et al.* 2012).

Table 2 Concentrations of DDT, HCH, PCB and PAH in soil, sediment, and organisms

	Location	Time	Depth	Composition	Concentration	Source	Reference
Soil	DDT						
	Two sides of modern and old course of the Yellow River, and Shen Xiangou basin	2007.5-2008.5	0-5cm	4	0.05-6 ng/g (0.85 ng/g)	Pesticides residues in the soil and new input from pesticide	(Yuan <i>et al.</i> 2012)
	Bincheng District in the Binzhou City	2009.9	0-20cm	6	63.8-315.6 ng/g (190.5 ng/g)	Past DDT usage and dicofol application	(Chen <i>et al.</i> 2011)
	Bincheng District in the Binzhou City	2009.9	0-15 cm	6	3.3-3819 ng/g	Past DDT usage (86.4%) and dicofol (13.6%) application	(Xie <i>et al.</i> 2012)
	Modern Course of the Yellow River	2008.8	0-15cm	4	1.23 ng/g	Agriculture usage and dicofol application, water and sediment transport and atmospheric deposition	(Zhang 2011)
	Middle Area of the Yellow River	2008.8	0-15cm	4	1.15 ng/g	Agriculture usage, water and sediment transport and atmospheric deposition	(Zhang 2011)
	Old Course of the Yellow River	2008.8	0-15cm	4	3.28 ng/g	History agriculture usage before 1976	(Zhang 2011)
	Nature Reserve of the Yellow River Delta	2012.7	0.20cm	4	0.17-10.46 ng/g	Long-term weathering of DDTs	(Da <i>et al.</i> 2014)
	HCH						
	Two sides of modern and old course of the Yellow River, and Shen Xiangou basin	2007.5-2008.5	0-5cm	4	0.04-1.19 ng/g (0.47 ng/g)	Pesticides residues in the soil and new input from pesticide	(Yuan <i>et al.</i> 2012)
	Modern Course of the Yellow River	2008.8	0-15cm	4	4.75 ng/g	Technical production, Pesticide residues, water and sediment transport and atmospheric deposition	(Zhang 2011)
	Middle Area of the Yellow River	2008.8	0-15cm	4	1.68 ng/g	Pesticide residues, water and sediment transport and atmospheric deposition	(Zhang 2011)
	Old Course of the Yellow River	2008.8	0-15cm	4	1.03 ng/g	Pesticide residues, water and sediment	(Zhang 2011)

	transport and atmospheric deposition						
	Nature Reserve of the Yellow River Delta	2012.7	0.20cm	4	0.28-1.32 ng/g	Historical sources and small amount of lindane	(Da <i>et al.</i> 2014)
	PCB						
	Bincheng District in the Binzhou City	2009.9	0-20cm	7	0-87 ng/g	Petrochemical industry (77.1%), municipal waste disposal (16.5%),	(Xie <i>et al.</i> 2012)
	Modern Course of the Yellow River	2008.8	0-15cm	9	9.3-65.4 ng/g (35.7 ng/g)	Waste capacitors and transformers' leakage, new input with sediment	(Zhang 2011)
	Middle Area of the Yellow River	2008.8	0-15cm	9	19.0-73.8 ng/g (29.5 ng/g)	Waste capacitors and transformers' leakage	(Zhang 2011)
	Old Course of the Yellow River	2008.8	0-15cm	9	15.6-124.2 ng/g (45 ng/g)	History production and usage before 1976	(Zhang 2011)
	Modern Yellow River Delta	2010	0-20cm	12	108.7-2152.7ng/kg	Water runoff (49.6%), point sources (25.1%), and atmospheric precipitation (8.4%)	(Liu <i>et al.</i> 2010)
	Modern YRD	2006.10	0-10cm	12	147.75-505.58 ng/kg	-	(Fan <i>et al.</i> 2009)
	PAH						
	East of the Hekou district, north shore of the Yellow River estuary		0-20cm	15	25.53-202.78 ng/g (99.38 ng/g)	Mixed source of petrogenic and pyrogenic	(Tao 2008)
	Modern Course of the Yellow River	2008.8	0-15cm	16	122.2-148.2 ng/g, (133.2 ng/g)	Mixed source of coal, wood and oil combustion	(Zhang 2011)
	Middle Area of the Yellow River	2008.8	0-15cm	16	153.0-228.9 ng/g, (192.1 ng/g)	-	(Zhang 2011)
	Old Course of the Yellow River	2008.8	0-15cm	16	126.5-198.9 ng/g, (148.7 ng/g)	-	(Zhang 2011)
	Bincheng District in the Binzhou City	2009.9	0-15cm	16	181.1-2176.0 ng/g, (359.8 ng/g)	Petroleum inputs for the urban and suburban areas, and biomass burning for the rural	(Xie <i>et al.</i> 2012)
Sediment	DDT						

	Lower stream of Yellow River and its tributary	2005.11	surface sediment	4	0.09-12.88 ng/g	-	(Sun <i>et al.</i> 2008)
	Old Yellow River Estuary	2012.7	surface sediment		0.04–1.07 ng/g	Historical residue	(Da <i>et al.</i> 2014)
	HCH						
	Lower stream of Yellow River and its tributary	2005.11	surface sediment	4	0.05-5.03 ng/g	-	(Sun <i>et al.</i> 2008)
	Old Yellow River Estuary	2012.7	surface sediment	4	0.00-14.85 ng/g	The technical historical residue and recent lindane	(Da <i>et al.</i> 2014)
	PAH						
	Yellow River Estuary	2006.8		25	48.56-277.12 ng/g, (122.92 ng/g)	Oil spill (74.5%), vehicles emission and natural gas burning (12.8%) and coking combustion (12.7%)	(Liu 2008)
	Southern YRD	2007.5	surface sediment	16	70.58-826.12 ng/ g (458.5 ng/g)	Oil source, mainly caused by petroleum	(Yuan <i>et al.</i> 2011)
	Northern YRD	2007.5	surface sediment	16	27.43-128.97 ng/ g (71.096 ng/g)	Anthropogenically induced	(Yuan <i>et al.</i> 2008)
	Yellow River Estuary and its adjacent areas	2003.9		16	371-650 ng/g	Oil pollution and combustion of fossil fuels	(Zhang 2008)
	Yellow River Estuary and its adjacent areas	2007.8		16	111.3-204.8 ng/g	Pyrogenic origin for the north and middle area, petrogenic and pyrogenic sources for the northwest	(Hu <i>et al.</i> 2010)
	Yellow River Estuary	2006.8		15	47.4-202.6 ng/g (101.6 ng/g)	Coal-fired (30.5%), wood combustion (27.7%), gasoline (17.5%) and diesel combustion (12.53%)	(Liu <i>et al.</i> 2009)
Organisms	DL-PCB						
	Modern YRD	2006.10	five plant species	12	2.32–287.60 ng/kg	Not from the soil but the air	(Fan <i>et al.</i> 2009)

There were only two studies related to OCPs residues in the surface sediments from the YRD (Sun *et al.*, 2008; Da *et al.*, 2014b). OCPs in twenty-three surface sediment samples from the middle and lower reaches of the Yellow River were analyzed. Correlations between OCP concentrations, the granularity of sediments, and total organic content (TOC) were discussed along with correlations among various components of the OCPs. OCP concentrations in sediment samples were in the range of 0.35-22.92 ng/g. Concentrations of HCHs and DDTs varied over 0.001-14.85 ng/g and 0.04-12.88 ng/g, respectively. Contamination levels of OCPs in sediment increased from the middle to the lower reaches along the Yellow River (Sun *et al.*, 2008). Strong correlations were found between the OCPs and clay particles percent (correlation coefficients $r=0.89$, $p<0.01$), TOC ($r=0.79$, $p<0.01$), hexachlorobenzene ($r=0.88$, $p<0.01$), HCHs ($r=0.95$, $p<0.01$), nonachlor ($r=0.87$, $p<0.01$), β -endosulfan ($r=0.94$, $p<0.01$) in sediments.

These correlations played an important role in determining the level of OCPs in the sediment. Correlations between HCHs and each of hexachlorobenzene ($r=0.80$, $p<0.01$), trans-chlordane ($r=0.99$, $p<0.01$), endosulfan pesticides ($r=0.75$, $p<0.01$) were also strong. These results indicated that the OCPs possibly have the same or similar sources and distribution mechanisms. The values of α/γ -HCH in sediment were in the range of 0-6.4, and the ratio of (DDE+DDD)/DDTs in the sediment core ranged from 0-0.87 (Da *et al.*, 2014b). Based on these ratio, HCHs contamination resulted from recent use of lindane. DDTs in this area were mainly due to residues from historical use in the region.

Occurrence of sediment PAHs in the wetland, riverine, estuarine environments and adjacent areas has been widely investigated (Table 2). In the sediments of Yellow River estuary, concentrations of sixteen PAHs varied from 27.43 ng/g to 1826.12 ng/g (average concentrations were from 71.093 to 458.5ng/g) (Yuan *et al.* 2008; Chen *et al.* 2011; Yuan *et al.* 2011). Nap and Phe comprised most of the PAH content in this area followed by Flu and Pyr.

Concentrations of low molecular weight 2-4 ring PAHs were high predominated over while PAHs with high molecular (5-6 ring) weight are lower (Hu *et al.* 2010). Among the different aquatic systems, relatively high levels of PAHs were found in sediments from the southern wetland and the Yellow River estuary (Zhang 2008; Yuan *et al.* 2011). PAHs measured from Bird Island originating from oil nearby an oil pumping unit, indicating that the pollution is mainly caused by petroleum (Yuan *et al.* 2011).

At this time, few studies have measured concentrations of POPs in biota from the YRD are available. No studies related to the OCPs and PAHs in biota in the YRD exist that we are aware of. Only two studies examined PCBs in biota. These studies examined accumulation of related to dioxin-like PCBs in plants (DL-PCBs) (Fan 2008; Fan *et al.* 2009). DL-PCBs are the most toxic group of PCB compounds. Though concentrations of DL-PCBs in environmental and biological matrices are generally low, they contribute much to the overall toxic value of PCBs. Fan *et al.*, (2009) investigated interspecies variance of DL-PCBs in plants from the YRD. Concentrations of 12 DL-PCBs congeners were examined in five plant species (including *Imperata cylindrical* var. major, *Phragmites australis* (Cav.) Trin. Ex Steud, *Suaeda Heteroptera*, *Tamarix chinensis* Lout., *Salix matsudana* Koidz) and their associated soils. Concentrations of DL-PCBs in plants were 575.48-819.23 ng/kg, and concentrations of DL-PCBs congeners in plants were 2.32-237.36 ng/kg. Plants in the sampling site of the YRD were not heavily polluted. DL-PCBs congener concentrations and ratios in plants greatly differed among species. The concentration of DL-PCBs in *I. Cylindrical* (575.48 ng/kg) was the lowest among the five species. The other four species were not significantly different from each other ($p < 0.05$). Two plants belong to the same family among the five species. *I. cylindrical* and *P. australis* had the smallest variance among the five species for accumulating DL-PCBs. Interspecies variance of all plants examined increased with increasing log *K_{oa}* of PCBs. Accumulation of DL-PCBs for annual plants was related to log *K_{oa}*, while for perennial plants it was independent of log *K_{oa}*.

There was no reported data related to the water POPs in the YRD.

Technical DDT and dicofol containing large amounts DDT-related compound impurities were the main sources of DDT pollution in China (Wang *et al.* 2005). Technical DDT is typically composed of 77.1% *p, p'*-DDT, 14.9% *o, p'*-DDT, 4% *p, p'*-DDE and some other trace impurities (Kannan *et al.* 1995).

Ratios of *o, p'*-DDT/*p, p'*-DDT ranged from 0.2 to 0.3 in technical DDTs and from 1.3 to 9.3 or greater in dicofol, respectively (Qiu *et al.* 2005). The two main DDT-related compounds, *p, p'*-DDE and *p, p'*-DDD, account for 71.98% of the total in the YRD. *p, p'*-DDT is largely degraded into *p, p'*-DDE or *p, p'*-DDD after years of microbial activity. In soil, DDT residues originated mainly from past agriculture usage. DDT in the environment is primarily transformed to the more stable metabolites DDD and DDE under anaerobic and aerobic conditions,

respectively, by either biotic (microbial conversion) or abiotic processes (i.e. chemical breakdown, photodegradation) (Bosch *et al.* 2015). Experiments have shown that approximately 66% of DDT applied to agricultural fields is transformed into DDE within one year (Cliath and Spencer 1972). A DDD/DDE ratio greater than 1 indicates that aerobic degradation is the main pathway of DDT loss. A ratio of less than 1 implies that the aerobic degradation is predominant (Wu *et al.* 2013). In general, a ratio of (DDE + DDD)/DDT greater than 0.5 indicates long-term biotransformation of DDT to DDE and DDD, while a ratio of less than 0.5 may indicate recent input of DDT (Hitch and Day 1992). Most (DDE + DDD)/DDTs ratios in YRD soils samples were greater than 0.5, implying the existence of aged DDT in the study area. However, the (DDE + DDD)/DDTs ratios in a few soil samples were less than 0.5, suggesting that there could be newer DDT inputs (Yuan *et al.* 2012). This newer input source of DDT was the pesticide 'dicofol' which is still widely used in the region to prevent the cotton bollworm. DDT was the raw material for industrial synthesis of dicofol, and because of this, often appears as an impurity in the dicofol product. Principal component analysis (PCA) and multiple regression analysis was used to identify the contaminated sources of DDTs (Xie *et al.* 2012). The analysis concluded that 86.4% of soil DDTs originates from past DDT usage, and 13.6% originates from dicofol application.

Technical HCH and lindane were two types of HCH products manufactured and used in China. Technical HCH contains about 55% to 80% α -HCH, 5% to 14% β -HCH, 8% to 15% γ -HCH and minor proportions of other isomers while the major component of lindane is γ -HCH (>99%) (Wang *et al.* 2009). Ratios of α/γ -HCH have been used to identify the presence of HCH or lindane in environmental media in the YRD (Zhang, 2011). For example, the α/γ -HCH ratio might be between 4 and 7 for the technical mixture, and nearly zero for lindane (Dai *et al.* 2011). Most sampling points in the Modern Course, Middle Area and Old Course of the Yellow River α/γ -HCH ratios are greater than 7 (Zhang 2011). However, it is worth noting that the α/γ -HCH ratio of two sampling points in the Modern Course and one sampling point in the Middle Area of the Yellow River was less than 1, indicating probable usage of lindane. The larger α/γ ratio might be due to the short half-life of γ -HCH in surface soil of only 2 months. It is possible that these are areas where the γ -HCH was degraded or bio-transformed completely. Additionally, HCHs in the YRD could have originated from pesticide residues and long-range atmospheric transport of pesticide residues (Gao *et al.* 2008).

Table 3 The correlation coefficients between the concentration of DL-PCBs and TOC, clay particles percent and sand particles percent

	TOC	Clay content	Sand content
Pearson's Coefficient	0.457	0.648	-0.472
<i>P</i>	<0.05	<0.01	<0.05

Production and usage of PCBs in the YRD mainly occurred before 1974. According to studies, the Modern Course of the YRD contains the highest levels of PCB contamination. Old Course contained more heavily chlorinated PCBs. Due to their high degree of chlorine substitution, heavily chlorinated PCBs exhibit poor migration and degradation ability. This property could explain why PCBs with heavy chlorination were more concentrated in the Old Course. Heavily chlorinated PCBs might have been deposited prior to the Yellow River diversion. Based on the rising trend of residual level of PCB 28 and PCB 52 in the Old course, Middle area and Modern course, these PCBs were deposited into the YRD after the Yellow River changed its course, even after PCBs went out of production. Other PCBs, such as PCB 153 and PCB 118 decreased in the Old course, Middle area and Modern course. It is possible that forbidden production of PCBs still played a limited role in PCBs degradation (Zhang 2011). Concentration of DL-PCBs had a slightly positive correlation with the TOC, a greatly significant positive correlation with clay content, and a significant negative correlation with sand content (Table 3). This result indicated that TOC, clay and sand contents in soil practical composition were the main influencing factors on the PCBs distribution (Liu 2008; Liu *et al.* 2010). Principle component analysis (PCA) was used to identify the contamination sources of PCBs (Liu *et al.* 2007). Principal component and multiple linear regression analysis suggested that soil PCBs most likely originate from the petrochemical industry (77.1%), municipal solid waste disposal (16.5%), local commercial PCB homologues usage (5.2%), and long-range atmospheric deposition (1.2%) (Xie *et al.* 2012).

Table 4 Literature values of selected molecular ratios of OCPs, PCBs and PAHs for various environmental sources

Pollutant	Characteristic indicators	Values and sources
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DDT	$m(p,p'\text{-DDE}+p,p'\text{-DDD})/$ $m(p,p'\text{-DDT})$ (Hitch and Day 1992) $m(o,p'\text{-DDT})/m(p,p'\text{-DDT})$ (Qiu <i>et al.</i> 2005)	> 0.5, long-term biotransformation of DDT to DDE and DDD 0.2-0.3, technical DDTs	< 0.5, recent input of DDT 1.3-9.3, dicofol
HCH	$m(\alpha\text{-HCH})/m(\gamma\text{-HCH})$ (Dai <i>et al.</i> 2011)	4-7, technical mixture	nearly zero for lindane
PAH	$m(\text{Ph})/m(\text{An})$ (Baumard <i>et al.</i> 1998) $m(\text{Fl})/m(\text{Fl}+\text{Pyr})$ (Yunker <i>et al.</i> 2002) $m(\text{IP})/m(\text{IP}+\text{BghiP})$ (Yunker <i>et al.</i> 2002) $m(\text{Baa})/m(\text{Baa}+\text{Chr})$ (Yunker <i>et al.</i> 2002) $m(\Sigma \text{LMW})/m(\Sigma \text{HMW})^a$ (Fernandes <i>et al.</i> 1997)	< 10, combustion origin > 0.4, combustion origin > 0.2, combustion origin > 0.35, combustion origin < 1, combustion origin	> 15, petroleum origin < 0.4, petroleum origin < 0.2, petroleum origin < 0.2, petroleum origin > 1, petroleum origin

a ΣLMW = sum of Nap, Acy, Ace, Fl, Ph, and An;

ΣHMW = sum of Flu, Pyr, Baa, Chr, BbF, BkF, BaP, IP, DBa, and BghiP.

The Shengli Oilfield, the second largest oilfield in China, is located in the YRD. Oil extraction and transportation leaks in the process can pollute the environment. C Petroleum coke and coal tar refining produce PAHs. Sites nearby oil pumping units had elevated levels of PAHs (Liu *et al.* 2008). If the concentration of PAHs in the soil is much higher than naturally occurring concentration, indicating that these soils are affected by human factors including chemical application, agricultural sewage sludge and accidental leakage, etc. Atmospheric wet and dry deposition plays a large role in PAH contamination (more than 90%) (Edwards 1983; Wilcke 2007; Yang *et al.* 2007).

Various methods exist to assess the dominant origins of PAHs. One method commonly used method employs molecular indices based on the ratios of individual PAH levels in soil such as Baa/(Baa+Chr) and Fl/(Pyr+ Fl) congener ratios (Yunker *et al.* 2002) (Table 4). According to ratio analysis (Ph/An, Fl/Fl+Pyr, IP/IP+BghiP, Baa/(Baa+Chr), *et al.*), PAHs contamination in the Yellow River Estuary showed a mixed PAH input pattern, including oil pollution, coal burning,

and wood combustion (Liu 2008; Tao 2008). Six main sources were established, including: oil and asphalt refineries, coal combustion, wood combustion, gasoline engine exhaust, diesel engine exhaust and oil spills. In the published paper, a chemical mass balance (CMB) model was established and source profiles were collected from the literature, effective and popular method to identify the origins of PAHs (US EPA 2004; Kim *et al.* 2013; Manoli *et al.* 2016). Coal and wood combustion are the two major sources of PAHs in the Yellow river estuarine area, whose relative contribution were 30.5% and 27.7%. Gasoline engine exhaust accounted for 17.49%, diesel engine exhaust, 12.53%, oil spills, 8.04%, and oil and asphalt refineries 3.73% (Liu 2008). The result of CMB model was consistent with that of factor analysis - multiple regression analysis (Liu *et al.* 2008). The factor analysis - multiple regression analysis indicated PAH contaminations in Yellow River Estuary area originated from coal and wood combustion, vehicles emission, oil spill, oil and asphalt refinery, which accounted for 41.89%, 27.43%, 10.76%, and 19.92% of PAHs respectively. Additionally, the PAHs have been compared with the individual PAHs concentrations, TOC content and particle size distribution. TOC of surface sediments in the Yellow River estuarine sediment were within the range of 0.86-2.85%, and the surface sediment was mainly comprised of silt. Multiple linear regressions showed that Pyr possessed the best linear relationship with the PAHs. Correlations of PAHs with particle size distribution and TOC were very weak which might be relatively low concentrations of PAHs in soils (Tao, 2008).

According to Chinese Environmental Quality Standard for Soils (GB15618-1995), soil can be classified as no DDTs pollution (< 50 ng/g), low DDTs pollution (50–500 ng/g), moderate DDTs pollution (500–1000 ng/g), and severe DDTs pollution (> 1000 ng/g). Concentrations of Σ DDT surveyed in the YRD in most samples were lower than the first grade (50ng/g), except samples in the Bincheng district in Binzhou City (Chen *et al.* 2011). In the Bincheng district, soil concentrations in eight samples (five samples from the rural area, two samples from the suburban area and one sample from urban area) reached the moderate pollution level, and three samples (two samples from the rural area and one sample from the suburban area) had severe pollution (Xie *et al.* 2012). DDT pollution levels in the rural area were significantly higher than in suburban and urban areas. Dutch soil guidelines and Canadian soil quality guidelines were also adopted to assess soil quality. The mean soil DDTs concentration in the YRD was far higher than the target value (10 ng/g), but lower than the intervention value (4000 ng/g) in Dutch soil guidelines

(VROM 2000). According to Canadian Soil Quality Guidelines for the Protection of Environment and Human Health, concentrations of DDTs in all soil samples in urban area were lower than the soil guideline value of 700 ng/g for residential and parkland soils. DDTs concentrations in 8.6% and 6.5% of soil samples from rural and suburban areas were higher than the soil guideline value of 700 ng/g for agricultural soils, respectively (CCME 2007). For soil HCHs, the concentrations of Σ HCHs in all reported samples were lower than the first grade (50ng/g). Thus, pollution levels of soil HCHs and DDTs in YRD were relatively mild. Two widely used sediment quality guidelines, i.e. the effects range-low value (ERL) and effects range-median value (ERM) guidelines (Long *et al.* 1995), as well as the threshold effects level (TEL) and probable effects level (PEL) guidelines (CCME 2002) were applied to evaluate the possible eco-toxicological risks of OCPs in the study area (Table 3). For DDTs, although levels did not exceed than ERM (46.1 ng/g) and PEL values (51.7 ng/g), partial sites in the study area were higher than ERL (1.58 ng/g) and TEL values (3.89 ng/g), suggesting that the exposure of DDTs may cause ecological risk on more sensitive organisms, such as the neighboring benthic organisms.

Table 5 Popular standards summaries for OCPs, PCBs and PAHs in China and abroad in various environmental media

Pollutant	Soil (ng/g)	Sediment (ng/g)			Water (ng/L)	Organism (ng/g)
DDTs	National Environmental Quality Standards for Soils of China (GB15618- 1995) (MEP 1997)	Canadian Sediment Quality Guidelines for the protection of aquatic life (CCME 2002)			Environmental Quality Standards for water of China (MEP 2002)	
	I <50 ^a		ERL ^b	ERM		
	II <500	DDE	2.2	27	DDTs, 1000	
	III <1000	DDD	2	20		-
		DDT	1	7		
		DDTs	1.58	46.1		
HCHs	National Environmental Quality Standards for Soils of China (GB15618- 1995) (MEP 1997)	Canadian Sediment Quality Guidelines for the protection of aquatic life (CCME 2002)			Environmental Quality Standards for water of China (MEP 2002)	
	I <50		ERL	ERM		
	II <500	γ -HCH	0.32	0.99	γ -HCH, 2000	-
	III <1000					
PCBs	Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health (CCME 2007)	Canadian Sediment Quality Guidelines for the protection of aquatic life (CCME 2002)			Environmental Quality Standards for water of China (MEP 2002)	Maximum levels of contaminants in foods (MHP 2005)
	Industry land, 50000		ISQG ^c	PEL ^d	PCBs, 8	PCBs 2000
	Leisure land, 5000	Freshwater sediment	34.1	277		
	Agriculture land, 500	Marine sediment	21.5	189		
PAHs	Classification of Soil Contamination (Maliszewska-Kordybach 1996)	Classification of Sediment Contamination (Baumard <i>et al.</i> 1998)			Environmental Quality Standards for water of China (MEP 2002)	Maximum levels of contaminants in foods (MHP 2005)
	I <200	I <100			Bap 2.8	Bap 5 for cereals;
	II <600	II <1000				10 for vegetable oil
	III <1000	III <5000				

a, I: non-contaminated soil, II: weakly contaminated soil; III: contaminated soil;

b, ERL: the effects range-low value;

c, ISQG: the interim sediment quality guideline;

d, PEL: the probable effect level.

In China, most PCB-containing equipment was stored at special disposal sites when they were taken out of use. The China State Environmental Protection Administration (SEPA) reported that directly polluted soils in some sealed storage locations reached as high as 4.54×10^6 ng/g, with levels in surrounding lands and farmlands having as much as 2930 ng/g (SEPA 2003). Along China's southeast coast, where some residents were illegally trading in or dismantling PCB-containing equipment, PCB concentrations have been found as high as 788 ng/g (Chu *et al.* 1995). Compared to the Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health (CCME 2007), all of the reported soil PCB values were lower than the standards for leisure land; however some reported PCB values were greater than the standards for agricultural land. Compared to the Union of Soviet Socialist Republics (USSR) Ministry of Health's allowable level of 60 ng/g for PCBs in ambient soil, all areas in the YRD had relatively larger PCB contamination levels on average (Bi *et al.* 2002). Agricultural soils sampled in suburban Beijing reported concentration levels of only 0.18 ng/g (Chu *et al.* 1995). Soils sampled from Shenyang, a major industrial city in north China's Liaoning Province, had PCB levels of 6.4–15.2 ng/g (Jing *et al.* 1992). While the pollution situation seems to be in control, the threat posed by seriously polluted point sources is concerning and should be a priority when assessing the risks identified by current data (Xing *et al.* 2005).

Risk assessment for PAHs in sediments has been well documented in the literature (Zhang *et al.*, 2012), and information is available on the qualitative risk assessment for PAHs. Natural background levels of soil PAHs generally range from 1 to 10 ng/g, and are mainly derived from the decomposition of plants and natural fires (Yang *et al.* 2007). Based on the reported results in the YRD, there were no soils with PAHs concentrationless than 10 ng/g. All of the soil tested has been subject to human influence, which is not surprising given the ubiquitous nature of PAHs. In China, concentration of the 16 PAHs in surface soils ranged from not detected to 151,600 ng/g, with the average of 3654.97 ng/g, the coefficient of variation was 4.44, with a median value of 580 ng/g. Due to the lack of PAH evaluation standards in China, concentrations of the 16 PAHs were also compared with the criteria put forward by Maliszewska-Kordybach (1996). Soil PAH contamination ranges were divided into four categories: unpolluted (<200 ng/g), weakly polluted (200–600 ng/g), moderately polluted (600–1000 ng/g), and severely polluted (>1000 ng/g). The concentrations of Σ PAHs in most samples were lower than the first grade (200ng/g), except

samples in the Bincheng district in the Binzhou City (Chen *et al.* 2011; Xie *et al.* 2012). In the Bincheng district in Binzhou City, all suburban soil, 94.3% of the rural soil, and 43.8% of the urban soil PAHs fell in the weakly polluted category. 37.5% and 18.7% urban sample concentrations fell in the moderately polluted category and severely polluted category, respectively (Xie *et al.* 2012). Therefore, it was determined that soil in this area has moderate PAHs pollution. According to Baumard *et al.* (1998), levels of sediment pollution by PAHs can be classified as low (10–100 ng/g), moderate (100–1000 ng/g), high (1000–5000 ng/g), and very high (5000 ng/g). According to these criteria, the levels of PAH in sediments samples could be classified from low (northern YRD) to moderate (other parts of YRD). Under the Canadian criteria of ERL (4022 ng/g) and ERM (44792 ng/g) (Long *et al.* 1995), all of the PAHs were lower than the ERL. Also, PAHs concentrations were at lower level in Yellow river estuarine compared with relevant areas worldwide in the published reports (Oliva *et al.* 2015). Compared soil PAHs in the YRD region with in some developed regions in China, concentrations were much lower than that in Beijing (suburban topsoil, 16 - 3884ng/g) (Ma *et al.* 2005), Hangzhou (59.71 - 615.8 ng/g) (Chen *et al.* 2004), and Hong Kong (urban soil 16 PAHs was 42.9 - 410 ng/g) (Zhang *et al.* 2006), but much larger than uncontaminated soil PAHs levels required by the Dutch government (20.0 - 50.0 ng/g) (Van Brummelen *et al.* 1996). Even so, soil PAHs contamination from petroleum deserves more attention, particularly near petrochemical production sites, In addition, PAHs from petroleum are more labile and can react with other pollutants to form more toxic derivatives. Although soil PAHs was generally in good condition compared to some other regions, the abnormally higher levels of soil PAHs still need vigilance (Cao *et al.* 2012).

A comprehensive assessment of the state of the POPs and spatial patterns in multiple environmental media in the YRD were conducted on a regional scale with the literature available. Levels of DDTs, PAHs and PCBs in soil and sediment samples were sufficient to cause potential ecological risk, but no negative effect was derived from the burden of HCHs. Spatial distribution of OCPs significantly increase along urban- rural gradient, while PCBs and PAHs showed opposite, which indicated a significant influence of agricultural, urban industrial practices, water and sediment transport and atmospheric deposition. Primary sources of DDTs, HCHs and PCBs mainly originated from the historical usage, new input of pesticide, and the petrochemical industry. PAH contamination was derived primarily from oil pollution and combustion of fossil

fuels. At this point in time, only qualitative ecological risk assessment of POPs is feasible due to lack of monitoring information and regulatory guidelines. Additionally, assessment of environmental fate focusing on atmospheric deposition, air-soil/water exchange, and riverine transport in the YRD was not available. Quantitative monitoring and transfer mechanism research programs would be useful to fill in the existing data gaps.

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Conflicts of Interest

The authors declare no conflict of interest.

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