

Concentrations, potential sources and behavior of organochlorines and phenolic endocrine-disrupting chemicals in surficial sediment of the Shaying River, eastern China

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Abstract Levels and distributions of organochlorine pesticides (OCPs) and phenolic endocrine-disrupting chemicals (EDCs) in surficial sediments of the Shaying River, the largest tributary of the Huaihe River in eastern China, were investigated to understand their relationship with the hydrodynamics. Concentrations of total hexachlorocyclohexane isomers (Σ HCHs) and dichlorodiphenyltrichloroethanes (Σ DDT) were in the range of 26.7–119 and 9.64–214 ng g⁻¹ with mean values of 104 and 80.7 ng g⁻¹, respectively. Residues of HCHs in sediments can be considered as originating from the application of both technical mixtures and lindane in the past. According to the spatial distribution of (DDD + DDE)/ Σ DDT ratios, the influence of recent DDT inputs was dominant upstream, whereas DDD prevailed downstream, due to anaerobic degradation. Concentrations of total phenolic EDCs (Σ EDCs) including nonylphenol (NP), octylphenol (OP) and bisphenol A (BPA) ranged widely from 425 to 3,953 ng g⁻¹ with the highest level occurring in the

middle reach. This accumulation could be attributed to the retransfer of surficial sediment from upstream, where the main sources are located. Spatial distribution of contaminants indicated that riverine hydrodynamics can significantly affect their behavior and fate in sediment. This evidence was further verified by multivariate statistical techniques such as Cluster Analysis (CA), Principle Component Analysis (PCA) and Discriminant Analysis (DA). The CA identified three distinct clusters reflecting the large complexity of river system like geography setting, hydrodynamic condition, etc. This finding was also confirmed by the DA. Furthermore, a PCA demonstrated that about 80.8 % of total spatial variance can be explained by the first three factors, which also indicated that contaminant spatial distributions are driven by local inputs, biodegradation and riverine hydrodynamics.

Keywords Organochlorine pesticides · Endocrine-disrupting chemicals · Sediments · Hydrodynamics · Shaying River (eastern China)

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Introduction

Urban, industrial and agricultural activities have released a large number of organic compounds to the aquatic environment. Among these anthropogenic organic contaminants, some of them are of a toxicological relevance, such as organochlorine pesticides (OCPs) and phenolic endocrine-disrupting chemicals (EDCs). They have been of great concern among the environmental researchers and the public opinion due to their ubiquity in aquatic environments and potential risks to wildlife and human beings (Sumpter and Johnson 2005). In China, OCPs, banned for use in 1983, were once commonly applied in agricultural

practices. However, phenolic EDCs, used as important industrial chemicals (e.g. surfactants), are not yet restricted. Recently, phenolic EDCs like nonylphenol (NP), octylphenol (OP) and bisphenol A (BPA), and OCPs such as hexachlorocyclohexane isomers (HCHs mainly include α -HCH, β -HCH and γ -HCH) and dichlorodiphenyltrichloroethanes (DDTs mainly include *p,p'*-DDT and its metabolites *p,p'*-DDE, *p,p'*-DDD) are still routinely detected in various environmental media including soil (Aigner et al. 1998; Zheng et al. 2009), sediment (Guo et al. 2009; Kim et al. 2009), air (Wania et al. 2003), water (Tauler et al. 2000), and organisms (Zhao et al. 2009).

Once entering into the environment, both phenolic EDCs and OCPs tend to distribute to soil, sediment or living organisms, especially where organic matter is abundant (Chen et al. 2006; Cailleaud et al. 2007; Fu et al. 2007) due to their high hydrophobic nature. Reported octanol–water partition coefficients ($\text{Log}K_{ow}$) were 3.40–4.48 for the three phenolic EDCs, 3.72–4.14 for HCHs, and 6.02–6.91 for DDTs, respectively (Navarro-Ortega et al. 2010; Willett et al. 1998). Therefore, the sediment is usually regarded as one of the most important reservoirs for these hydrophobic organic contaminants and also a potential secondary source to the environment. That is, with declining use of these contaminants, their burden in water body would also reduce, and what is stored in sediments may be released into the overlying water (Wu et al. 1999; Liu et al. 2008). Furthermore, the transfer of hydrophobic organic contaminants such as OCPs from sediment to organisms was also regarded as a major route of exposure for many species (Zoumis et al. 2001). Consequently, clarifying the residual levels of OCPs and phenolic EDCs in sediments remains important to understand their environmental behavior, and assess their potential risks to aquatic organisms (Navarro-Ortega et al. 2010).

Although the occurrences of OCPs and phenolic EDCs in sediment of rivers have been reported, the knowledge on behavior and fate of these chemicals in the Huaihe River basin, one of seven main rivers in China, remains limited. As a high-regulated river system with many floodgates throughout the whole basin, the flow regimes of the main stream and its tributaries have been controlled (Zhang et al. 2011a). However, information on the influence of hydrodynamics on behavior of OCPs and phenolic EDCs in sediment was rarely reported (Funakoshi and Kasuya 2009). Therefore, to understand spatial distribution, potential sources and behaviors of OCPs and phenolic EDCs in sediment of the Shaying River, one of tributaries of the Huaihe River, were chosen. The objectives of this paper were (1) to assess concentrations and distributions of OCPs and phenolic EDCs in sediment along the river, (2) to analyze the compositional characteristics of OCPs and phenolic EDCs in sediment to locate the possible sources,

and (3) to understand the potential influence of riverine hydrodynamics on the behavior and fate of the hydrophobic pollutants.

Materials and methods

Site descriptions and sample collections

Originating from Xinmi County, Henan Province, the Shaying River flows through the cities of Zhengzhou, Zhoukou, and Fuyang then down into the main stream of the Huaihe River near Mohekou in Anhui Province (Fig. 1). The length of the river is 620 km and its basin area is 40,000 km². Annual mean temperature in the basin ranges from 14 to 16 °C and the average annual rainfall is 770 mm. The Shaying River mainly consisted of the Jialu River, Ying River and Sha River, which merge near the Zhoukou city. About 50 km downstream of the confluence, Shenqiu floodgate was built as one of the most important floodgates in the river in the 1970s.

The Shaying River, the largest tributary of the Huaihe River (about 14 % of the total drainage area), has been undergoing rapid urbanization and industrialization in the last decades, facing massive discharge of wastewater and declining surface water quality. Monitoring data showed more than one-third of the total COD and NH₃-N in the Huaihe River basin were contributed by the Shaying River (Dong and Mao 2005). Furthermore, 18 priority organic pollutants listed by US EPA were found in groundwater upstream of the Shaying River, the Jialu River basin, according to the survey on the water quality carried out in 2004 (Wang et al. 2004). Zhengzhou city is the biggest city in the upper stream, having a long history of textile and metallurgical industries. Zhengzhou city mainly discharged domestic and industrial wastewaters with a significant content of phenolic EDCs (Zhang et al. 2009). Furthermore, HCHs and DDTs were extensively used in the Shaying River basin, as it is an important agriculture area, to protect crops from pests and control malaria (Liu et al. 2008). Human activities have posed a significant threat on the aquatic ecosystem and residues of anthropogenic organic contaminants in sediment can be regarded as the integrated result of both long-term accumulation and current inputs. However, the knowledge of concentrations, sources and behavior of phenolic EDCs and OCPs in sediment of this waterway is very poor. For this study, surficial (top 5 cm) sediments were collected along the river using a stainless steel small-volume grab sampler in September 2007. Samples were placed in pre-cleaned glass bottles and stored in the refrigerator at –20 °C. The global positioning system (GPS) was used to locate the sampling sites.

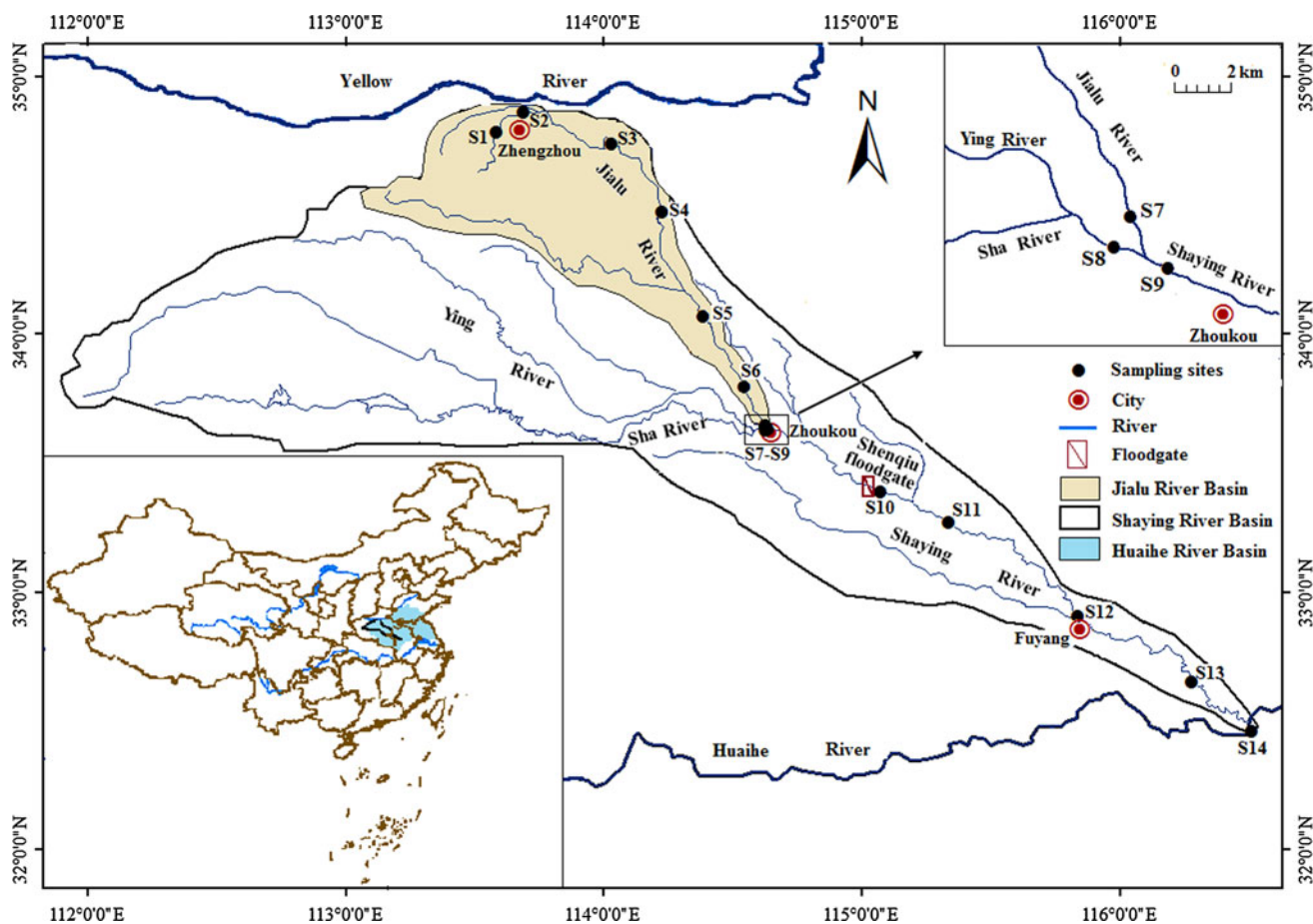


Fig. 1 Sampling sites location in the Shaying River Basin

Analytical procedure

All solvents used for sampling and analysis were HPLC grade: 4-*tert*-octylphenol was purchased from Wako Pure Chemical Industries (Japan), 4-nonylphenol (mixture of compounds with different isomers) was obtained from Tokyo Chemical Industry, Japan, and *p,p'*-DDE, *p,p'*-DDD, *p,p'*-DDT, and α -HCH, β -HCH, γ -HCH were purchased from the center of standard material of Agricultural Ministry, China. Internal standards containing phenanthrene-*d*₁₀, pentanitrobenzene (PCNB) and 2,4,5,6-Tetrachloro-*m*-xylene(TMX) were purchased from Accu Standard, Inc. (USA). The Florisil® (60–200 mesh, USA) was activated at 650 °C for 3 h and deactivated at 130 °C for 12 h, then the Florisil® was cooled in desiccators and after it, ultrapure water (5 %, w:w) was added. To remove organic contaminants, all the glassware used for organic compounds analysis were baked for 4–5 h at 450 °C prior to use.

Dried sediment samples (10.0 g) were ultrasonically extracted three times for 20 min with 20 ml of acetone:methanol (1:1, v/v) for phenolic EDCs and hexane:acetone (1:1, v/v) for OCPs, respectively. Extracts were centrifuged for several minutes at >3,000 rpm, and

then concentrated to 1–2 ml with rotary evaporator at 35 °C. Florisil columns (1 cm i.d.) were used for clean-up of all the concentrated extracts. OCPs were eluted with 10 ml hexane/DCM (7:3, v/v) and phenolic EDCs with ethyl acetate. Both solutions were evaporated to 1 ml in a vial and an appropriate volume of the internal standard, PCNB for OCPs and phenanthrene-*d*₁₀ for phenolic EDCs, was added prior to GC–MS analysis.

Phenolic EDCs and OCPs were analyzed using Gas chromatography–mass spectrometry (Shimadzu GC-2010, Shimadzu MS-Parvum2). A Rtx-5MS fused silica capillary column (30 m, 0.25 mm i.d., and 0.25 μ m film thickness) was employed with helium as carrier gas at a constant flow rate of 1 ml min⁻¹. The GC inlet temperature and MS interface temperature were maintained at 250 and 310 °C, respectively. For phenolic EDCs, the GC oven temperature was held at 70 °C for the initial 2 min, then programed at 30 °C min⁻¹ to 180 °C, 2 °C min⁻¹ to 200 °C, 30 °C min⁻¹ to 310 °C, and held constant for 10 min. For OCPs, the oven temperature was held at 80 °C for the initial 2 min, then programed at 10 °C min⁻¹ to 180 °C, 2 °C min⁻¹ to 200 °C, 30 °C min⁻¹ to 280 °C, and held constant for 10 min. Sample (1–2 μ l) was injected in

splitless mode. The MS was operated in full-scan mode from m/z 50–500 for qualitative analysis, and quantitative analysis was carried out in SIM mode.

In addition, sequential loss on ignition (LOI) method is used to estimate the total organic carbon (TOC) of sediments (Dean 1974). Briefly, about 20.0 g of sediment was dried to constant weight at 105 °C and then heated at 550 °C for 1 h to combust the organism matter to carbon dioxide (Heiri et al. 2001). The relationship between TOC and LOI at 550 °C was described as $\text{TOC} (\%) = 0.458 \times \text{LOI} (\%) - 0.4$ (Xue et al. 2006). Three replicates were carried out to determine the variation and the mean value of TOC was adopted.

Quality assurance and quality control (QA/QC)

The calibration curve was determined with seven different concentrations of working standards, and a good linearity was observed ($r^2 \geq 0.99$). The method detection limits (MDL) were taken to be 3:1 signal-to-noise ratio (S/N) and ranged from 14.1 to 32.5 ng g⁻¹ for phenolic EDCs and from 1.81 to 5.88 ng g⁻¹ for OCPs. Recoveries were checked through three replicate analyses of samples spiked with known levels of all target compounds (200 ng g⁻¹). These replicates were prepared and processed as described in analytical method. Recoveries of phenolic EDCs and OCPs were in range of 72.0–83.5 and 76.8–98.4 %, respectively. For every batch of ten samples, a solvent blank and a procedural blank were run in sequence to check contamination. According to the results ($n = 3$), there was no blank correction to be performed since no phenolic EDCs and OCPs were detected. Triplicate analyses of each sediment sample were processed with relative standard deviation (RSD), 4.8–15.2 % for phenolic EDCs and 3.9–11.2 % for OCPs, respectively. Furthermore, samples showing high concentrations were repeatedly performed to further validate the results.

Multivariate statistical analysis

Multivariate statistical techniques were widely applied to extract hidden significant environmental information and distinguish the different contaminant sources (Simeonov et al. 2003). Facchinelli et al. (2001) used Cluster Analysis (CA) and Principle Component Analysis (PCA) to predict potential non-point heavy metal pollution sources in soils of Italy at a regional scale. In general, CA is used to demonstrate the specific links between sampling points, while PCA can be performed to identify the ecological aspects of contaminants in environmental system (He et al. 2001; Tauler et al. 2000).

In this study, the descriptor variables (pollution indicators) were block standardized using Eq. (1) prior to CA to

avoid effects of units dimensions, whereas the CA was carried out using the square euclidean distance measurements obtained by Eq. (2) (Kowalkowska et al. 2006):

$$Z_{ji} = (X_{ji} - X_j) / S_j \quad (1)$$

$$d_{ij}^2 = \sum_{k=1}^m (Z_{i,k} - Z_{j,k})^2 \quad (2)$$

Where Z_{ji} and X_{ji} are the standardized and original measured values, respectively; X_j and S_j are the average value and standard deviation of variable j . $d_{i,j}$ denotes the Euclidean distance, $Z_{i,k}$ and $Z_{j,k}$ are the values of variable k for object i and j , respectively, and m is the number of variables.

The PCA performs a pure mathematical decomposition of the data by producing principal components (PC) with some constraints like orthogonality (Tauler et al. 2000). PCA bilinear model can be written using the following matrix decomposition equation (Navarro-Ortega et al. 2010; Ouyang 2005):

$$X = TP^T + E \quad (3)$$

Where X , the data matrix (e.g. sediment concentrations of OCPs and phenolic EDCs in this study), is decomposed into a long augmented matrix T (scores matrix) and a loading matrix P^T (Stanimirova et al. 2005). In this study, the dimensions of T and P^T were $14 \times N$ with $N \times 10$ (N is the numbers of PCs; 14 and 10 represent the numbers of samples and variables), respectively. The matrix E contains the residual data variations, not modeled by the principal components, thus having the same dimensions as matrix X .

Furthermore, Discriminant Analysis (DA) is also applied to determine the variables that could discriminate different groups by building up a discriminant function (Shrestha and Kazama 2007):

$$f(G_i) = k_i + \sum_{j=1}^n w_{ij} p_{ij} \quad (4)$$

Where i is the number of groups (G), k_i are the constants inherent of each group, n is the number of parameters used to classify a set of data into a given group, w_j is the weight coefficient, assigned by DA to a given selected parameter (p_j). Multivariate statistical analysis was performed using the SPSS 13.3 software for Windows.

Results and discussion

Concentrations and spatial distributions of OCPs and phenolic EDCs

Table 1 summarizes analytical data (minimum and maximum concentrations) and some useful parameters as median and mean values. These latter, except for TOC%

Table 1 Descriptive statistics of variables measured in the river

	N	Minimum	Median	Maximum	Mean	SD	TEL (% >TEL)	PEL (% >PEL)	CSQ (% >CSQ)
TOC%	14	0.28	2.61	4.14	2.29	1.23			
α -HCH	14	<2.9	18.52	32.0	18.1	9.88			
β -HCH	14	7.20	28.9	58.4	30.9	18.2			
γ -HCH	14	13.4	29.5	52.4	31.7	11.4	0.3 (100)	1 (100)	35 (35.7)
<i>p,p'</i> -DDE	14	1.16	4.86	8.11	5.00	1.83	2.1 (92.3)	374.2 (0)	
<i>p,p'</i> -DDD	14	6.69	32.4	57.6	30.2	18.4	1.2 (100)	7.8 (92.3)	
<i>p,p'</i> -DDT	14	1.80	52.7	166.2	69.1	65.2	1.2 (100)	4.8 (642)	
OP	14	15.9	31.1	49.7	30.4	10.3			
NP	14	85.0	210	422	233	106			1.4 (100)
BPA	14	274	1,645	3,534	1,899	1,055			
Σ EDCs	14	425	1,834	3,953	2,162	1,104			
Σ HCH	14	26.7	75.7	119	80.7	30.3			
Σ DDT	14	9.6	87.1	214	104	82.2	3.9 (100)	51.7 (57.1)	
Σ OCPs	14	36.4	149	331	185	108			

TEL Threshold effect level, PEL Probable effect levels, CSQ Canadian sediment quality guidelines

and α -HCH, were always greater than the median value indicating that the data were skewed towards high concentrations. Furthermore, the standard deviations of all variables were of the same order of magnitude of the mean values, thus indicating the existence of significant spatial differences of contaminant concentrations in different reaches along the river.

DDTs were detected in all sediment samples, which suggested that they were widely distributed in sediment of the Shaying River. The concentrations were in range of 1.80–166 ng g⁻¹ for DDT, 6.69–57.6 ng g⁻¹ for DDD and 1.16–8.11 ng g⁻¹ for DDE, with average values of 69.1, 30.2, and 5.0 ng g⁻¹, respectively. HCHs were in the ranges <1.81–32.0 ng g⁻¹ for α -HCH, 7.20–58.4 ng g⁻¹ for β -HCH and 13.4–52.4 ng g⁻¹ for γ -HCH with average concentrations of 18.1, 30.9, and 31.7 ng g⁻¹, respectively. Like DDTs, the average concentration of HCHs upstream of the river was higher than downstream (S10–S14) and their average ratios (Conc._{Upstream}/Conc._{Downstream}) were 1.06 for α -HCH, 2.86 for β -HCH and 1.19 for γ -HCH, respectively.

Concentrations of phenolic EDCs in sediments were 15.9–49.6 ng g⁻¹ for OP, 85.0–421 ng g⁻¹ for NP and 273–3584 ng g⁻¹ for BPA, with average values of 30.1, 237, and 1916 ng g⁻¹, respectively. Their presence increased gradually from the upper stream to middle stream (S5–S9) with a peak occurring at site S6. Because the Zhengzhou urban zone is considered as the major source of phenolic EDCs (Zhang et al. 2009), their accumulation in sediment of the middle stream could mainly derive from the transfer of surface sediment from the upper stream.

Interestingly, the concentrations of both OCPs and phenolic EDCs in samples S9, downstream of the

confluence, and S8, upstream of the confluence, showed similar characteristics (Fig. 2), significantly different from those of the Jialu River sample (S7). Some studies showed that the tributary influxes of sediment increased with the size of the tributary relative to the main stem (Benda et al. 2004). Thus, these results might be due to the impact of hydrodynamic conditions on the accumulation of organic contaminants: the annual flow of the Shaying River (125.5 m³ s⁻¹) near site S9, being four times higher than that of the Jialu River near site S7 (20.4 m³ s⁻¹). Furthermore, concentrations of OCPs and phenolic EDCs showed significant differences upstream and downstream of the Shenqiu floodgate (1 km upstream of S10) with the higher values occurring upstream (Fig. 2). The result indicated the potential influence of the floodgate on the

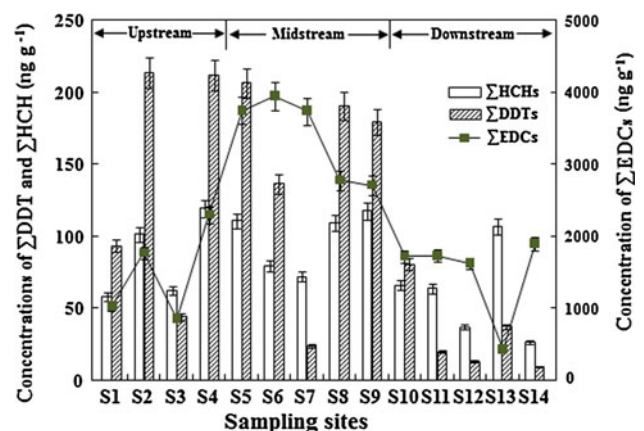


Fig. 2 Concentrations of total phenolic EDCs, DDTs, and HCHs in sediment (ng g⁻¹) of all sampling sites along the river. Mean of repeated analyses was plotted with one standard deviation

downstream transport of organic contaminants in sediment, which might be limited by the change in the flow regime that cause more deposition of surficial sediment and suspended particle materials (SPM) upstream of the floodgate.

Potential risks of phenolic EDCs and OCPs

There were few sediment quality standards established for OCPs and phenolic EDCs in China (Sun et al. 2010). Therefore, to evaluate the potential risk of sediment to aquatic organisms in the Shaying River, measured concentrations were compared with widely used sediment quality guidelines. The Canadian ones (CSQ; CCME 2002) provided limits for 33 compounds like HCHs, DDTs and NP for different types of sediments to protect aquatic life. Furthermore, threshold effect level (TEL) and probable effect levels (PEL) are used to predict biological effects of contaminated sediments (e.g. Long et al. 1995). Accordingly, TEL is the value representing the concentration below which adverse biological effects are expected to occur rarely, whereas PEL denotes the concentration above which adverse effects are expected to occur frequently (CCME 2002; Chapman et al. 1998).

Selected sediment quality guidelines are also summarized in Table 1. The concentrations of DDTs in most samples were above the PEL, which indicated that adverse effect may be caused by these compounds. Meanwhile, sediment concentrations of DDD and DDT were higher than the values of PEL at 13 sites (except S14) and 9 sites (except S11–S14), respectively. Concentrations of γ -HCH were higher than PEL at all sites. Moreover, about 36 % of all sites showed concentrations of γ -HCH greater than the values of CSQ (35 ng g⁻¹) and the lowest γ -HCH concentrations of 13.4 ng g⁻¹ greatly exceeded the PEL limits. A similar trend was found for NP with concentrations in sediment at all sites higher than respective value of CSQ.

The results indicated that these compounds may cause adverse biological effects throughout the whole Shaying River and attention should be paid even though the use of these chemical has been banned for several decades now.

Pairwise correlations between different variables

Correlations analysis of different variables can improve our understanding of the environmental behavior and fate of contaminants by demonstrating their relationships. Pairwise correlations between all the variables measured in this study are showed in Table 2. Strong positive correlation between TOC% and DDD, DDT, β -HCH was found ($p < 0.01$; $n = 14$) indicating that their accumulation in sediments was closely related with organic matter content. Meanwhile, the three compounds also had good positive correlations between each other ($r > 0.80$; $p < 0.01$; $n = 14$). These evidences suggest that the three OCPs could have been used together in field or rather they underwent a similar behavior in the environment and fate in sediments. Moreover, the highly positive correlation between DDD and DDT showed that the DDD residue in sediment mainly derive from the anaerobic degradation of DDT. DDE and NP had moderate positive correlations with TOC% ($p < 0.05$; $n = 14$), with coefficients of 0.57 for DDE and 0.60 for NP, which suggested that the organic carbon may play an important role in controlling their accumulation in sediments.

γ -HCH had a good positive correlation with β -HCH ($p < 0.01$; $n = 14$) and a moderate positive correlation with α -HCH ($p = 0.25$; $n = 14$) indicating that either these isomers might come from the common source (e.g. the application of the technical mixture of HCH in cropland) or that a transformation of γ -HCH to α/β -HCH may occur in sediments. Compared with the DDT family, HCHs had a lower correlation with TOC%, which can be

Table 2 Pairwise correlation coefficients between the variables measured in the river

	TOC %	α -HCH	β -HCH	γ -HCH	<i>p,p'</i> -DDE	<i>p,p'</i> -DDD	<i>p,p'</i> -DDT	OP	NP	BPA
TOC %	1									
α -HCH	0.257	1								
β -HCH	0.824**	0.086	1							
γ -HCH	0.491	0.327	0.678**	1						
<i>p,p'</i> -DDE	0.570*	0.53	0.524	0.572*	1					
<i>p,p'</i> -DDD	0.763**	0.051	0.928**	0.710**	0.422	1				
<i>p,p'</i> -DDT	0.866**	0.038	0.897**	0.589*	0.508	0.797**	1			
OP	-0.546**	0.037	-0.46	-0.42	-0.398	-0.38	-0.695**	1		
NP	0.602*	-0.075	0.297	-0.084	0.048	0.31	0.44	-0.106	1	
BPA	0.429	0.169	0.414	-0.09	-0.141	0.336	0.325	-0.051	0.317	1

** Correlation is significant at the 0.01 level (2-tailed)

* Correlation is significant at the 0.05 level (2-tailed)

explained by the fact that the water solubility and volatility of HCHs are generally higher than those of DDTs (Willett et al. 1998). Generally, the relationships between phenolic EDCs and OCPs were low and the correlations among phenolic EDCs were also poor, indicating the diversity of their chemical properties and source patterns, with the point source discharges for phenolic EDCs and non-point sources for OCPs in the basin. Although some studies have reported that the adsorption of organic contaminants to sediment is related with sediment’s organic carbon contents (Johnson et al. 1998), it was noted that a significant negative correlation of TOC% and OP existed in the basin ($r = -0.54; p < 0.05, n = 14$). Some studies also reported that the TOC distribution correlated well with the grain size of sediments that, in turn, is influenced by the hydrodynamics in the river (Hu et al. 2009). If so, the accumulation of OP in sediment might be a function of the proximity of the sources and less by the distribution driven by hydrodynamics.

Potential sources and behavior of OCPs and phenolic EDCs

The compositional characteristics of organic contaminants in the sediment can provide information about their environmental behavior (inputs, interactions, transport, accumulation and biodegradation). The composition of DDTs in sediment (Fig. 3) showed a predominance of DDT (11.89–77.8 %), followed by DDD (15.7–69.3 %) and DDE (2.02–24.0 %), with average proportions of 49.0, 41.5, and 9.5 %, respectively. The concentration ratios between DDT and its metabolites can provide information on its application history, because DDT can be gradually transformed to DDE in aerobic condition or DDD in anaerobic condition (Liu et al. 2008). In general, lower

$(DDE + DDD)/\sum DDT$ and higher $DDT/\sum DDT$ (DDT fraction) ratios indicate recent use of DDT. Some studies take 0.5 as an arbitrary value of the ratio of $(DDE + DDD)/\sum DDT$ to distinguish between historical and recent application (Hitch and Day 1992). In the study, a low DDE/DDD ratio (<0.5) was found, indicating that anaerobic condition can occur in sediment of the Shaying River. In addition, the ratios of $(DDE + DDD)/\sum DDT$ in upstream and middle stream sediment samples were lower than 0.5, whereas the ratios become higher downstream, after the Shenqiu floodgate (Fig. 3). Furthermore, a significant positive correlation between $DDT/\sum DDT$ ratios and concentrations of $\sum DDT$ in upstream and middle stream sediment was found with the correlation coefficient (R) of 0.72. The results indicated that there are recent inputs of parent DDT, which do not undergo significant degradation in sediments of these reaches.

Compositional differences of HCH isomers can also be used to identify the possible contamination sources (Iwata et al. 1995; Liu et al. 2008). The technical mixture of HCHs, a widely applied broad-spectrum pesticide in China during 1950–1980, typically contained 71 % of α -HCH, 6 % of β -HCH, 14 % of γ -HCH and 9 % of δ -HCH (Tao et al., 2008). Lindane (>99 % γ -HCH) was also used for another decade (1970s–1983). Although α -HCH/ γ -HCH ratios were about 4–7 in technical mixture of HCHs, the ratios in area where lindane has been typically used would be in range of 0.2–1.0 owing to the photochemical transformation of γ -HCH to α -HCH (McConnell et al. 1993). In this study, the α -HCH/ γ -HCH ratio in all sediment samples were lower than 1.28, with an average value of 0.60. Moreover, the average γ -HCH content among total HCHs in sediment was 40.5 %, higher than the 14 % contribution of the γ isomer to the technical grade mixture. These results indicated that both technical mixture and lindane had been widely applied in this catchment.

The average composition of HCHs also showed that β -HCH (36.1 %) and γ -HCH (40.5 %) were the dominant HCH isomers in all sediment samples from the Shaying River. In general, β -HCH is regarded as the most persistent isomer, owing to its lower vapor pressure of 4.8×10^{-2} MPa (25 °C), water solubility of 0.24 mg l^{-1} and metabolic activity (Willett et al. 1998; Hu et al. 2009). It should be noted that γ -HCH can be transformed to α -HCH, which can be further transformed into β -HCH in the aged environmental samples (Walker et al. 1999). Thus, the accumulation of β -HCH in sediments would be also derived from the long-term degradation of HCHs. In addition, the relative concentrations of α -HCH to β -HCH are often used to distinguish the historical residues from recent application (Tao et al. 2008). In this study, α/β -HCH ratios in sediment were in the range of 0–2.25 with the average value of 0.86 (Fig. 4). Compared with the α -HCH/

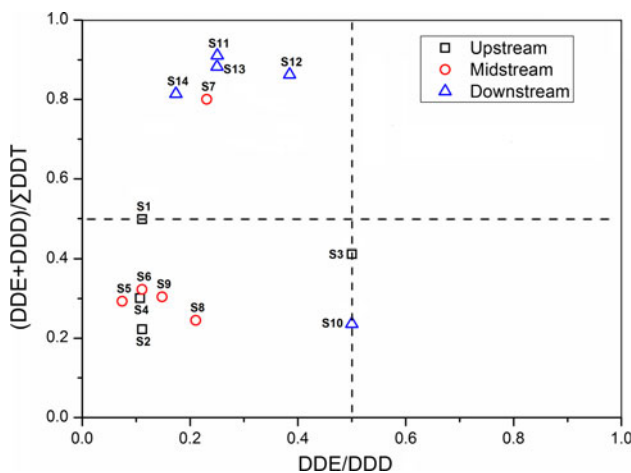


Fig. 3 Compositional characteristics of DDTs in sediment of all sampling sites

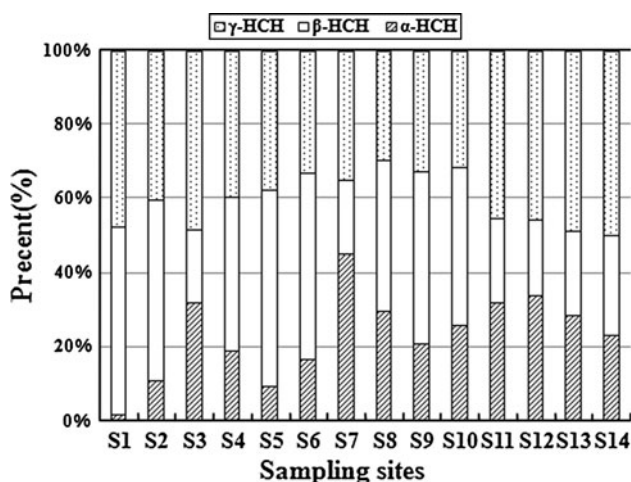


Fig. 4 Compositional characteristics of HCHs in sediment of all sampling sites

β-HCH ratio in technical mixtures (11.8), it is reasonable to consider that HCHs in sediment of the Shaying River basin might have undergone a relatively long-term degradation.

To understand the compositional characteristics of phenolic EDCs in sediments, the ratios BPA/OP and NP/OP at different sampling sites along the river were plotted in Fig. 5. Both ratios increased from downstream of the Zhengzhou urban zone (from S1 to S3). This means that more BPA and NP rather than OP were discharged. After S4, both BPA/OP and NP/OP declined along the river and the slope coefficient of the trendline (4.07) shows that the decrease of BPA concentrations was greater than that of NP and that the effect for these chemicals was higher than for OP. These results can be explained by the different water solubility of the three compounds, which is in the order: BPA (210 mg l⁻¹ in 25 °C) > NP (6.0 mg l⁻¹ in 25 °C) > OP (1.2 mg l⁻¹ in 25 °C) (Tan et al. 2007). This means that more BPA and NP than OP can re-dissolve into the aqueous phase from bottom sediment or re-suspended particles.

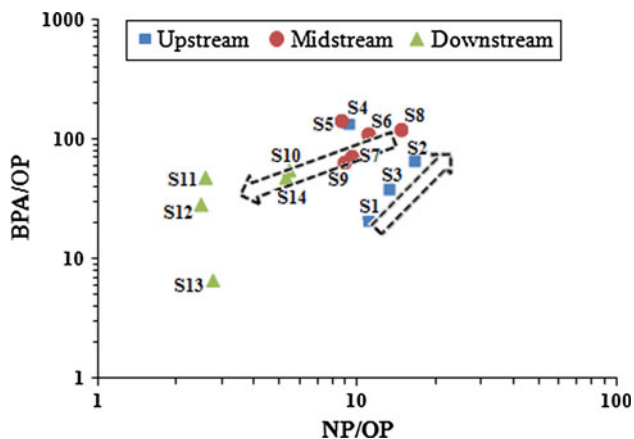


Fig. 5 Plot of BPA/OP vs. NP/OP in sediment of all sampling sites

Factors driving contaminant distributions

A Cluster Analysis based on the variables of TOC%, DDT, HCH and phenolic EDCs data grouped all 14 sampling sites into three clusters with $(D_{link}/D_{max}) \times 25 < 10$. The result of classification was illustrated by a dendrogram in Fig. 6. Cluster 1 is composed by sites S3, S10–14, mainly located downstream of the Shenqiu floodgate except site S3 (Fig. 1). The inclusion of the upper stream sampling site S3 in cluster 1 indicated that it was also characterized by the low concentrations of β-HCH, DDD, DDT, NP and BPA. The hydraulic gradient in the reach of S2–S3 was 0.42 ‰, greater than that of the other reaches. This means that a faster flow velocity might bring away fine sediment particles and water soluble compounds such as NP and BPA downstream, where accumulation may be favored in the downstream of S3. Meanwhile, the rapid flow also makes the accumulation of persistent contaminants like β-HCH, DDD and DDT difficult, thus explaining the low levels of these contaminants in S3. In addition, the low residue levels of these organic contaminants in sediment downstream (S10–14) may be due to the Shenqiu floodgate that makes the downstream transport of particles and associated contaminants more difficult.

Cluster 2 is formed by sites S2, S4, S5, S8 and S9 that shows high concentrations of DDD, DDT and the low $(DDD + DDE)/\sum DDT (<0.31)$ ratios, which indicated that the level of this contamination was serious and that DDT did not undergo degradation for a long period. Site S2, located 2 km downstream of the Zhengzhou urban zone, receives the largest amounts of wastewaters from the city (Zhang et al. 2011b) and the pesticide dicofol containing high impurities of DDT compounds was produced in four plants in the Zhenzhou industrial area. The high DDT concentrations detected at S2, S4 and S5 may have been caused by a recent discharge of the wastewater from the urban zone (<http://www.chinapopsorg/guide/px/pxcl/bah/>). The sites grouped in cluster 3 (S1, S6, and S7) had a relatively low concentration of HCHs.

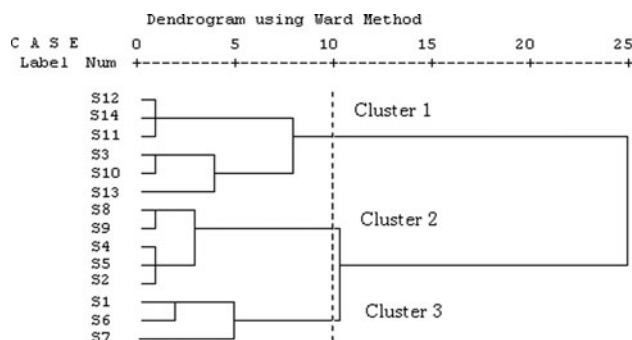


Fig. 6 Dendrogram showing clustering of sampling sites based on variables measured in sediment of the river

Principle Component Analysis was used to explore the potential driving factors of spatial distribution for OCPs and phenolic EDCs in sediment of the river. Only the first three principal components (PCs), representing 80.8 % of the total variance, were taken into consideration (Fig. 7). The first PC, which explained 50.4 % of the total variances, has high loading of DDD and DDT: 0.88 and 0.89, respectively, whereas the loading of DDE (0.55) was significantly lower. DDT would be easily biodegraded into DDD under anoxic condition, and this is why they appeared together in PC1 with similar loadings. Generally, PC1 had the high loadings with TOC% and OCPs, excepting α -HCH, an information consistent with the correlation coefficients. As mentioned above (Figs. 3 and 4), a long-term biodegradation from γ -HCH to β -HCH and from DDT to DDD/DDE occurred in the sediments. Therefore, PC1 describes a non-point sources related with OCPs reflecting the long-term accumulation and biodegradation of these compounds in sediment.

The second PC explained 17.5 % of the total variance having positive loadings of phenolic EDCs, DDD, and DDT. High positive loadings of NP and BPA were found in PC2 with values of 0.82 and 0.84, respectively. Phenolic EDCs were mainly derived from the effluent of sewage treatment plants (STPs) and were released from both

industrial and domestic plastic products. Despite the official ban of DDT in 1983, the produce and usage of dicofol, with high impurity of DDT, have been allowed in the basin until recently. This may have been an important source for present DDT sediment contamination. There were four pesticide plants producing dicofol in the Zhengzhou urban zone (<http://www.china-pops.org/guide/px/pxcl/bah/>). Thus, PC2 related with contaminant point source such as wastewaters discharged from local STPs.

The third PC explained 12.9 % of the total variance and had high positive loadings for DDE and α -HCH (>0.72). The moderate correlation between PC3 and γ -HCH had a loading of 0.48. Locations with high PC3 scores, principally sites S7–S9 near the confluence, favored deposition of more suspended particles and reduction of river flow. Thus, α -HCH and γ -HCH, in spite of their high water solubility, adsorbed into suspended particles and were further sedimented in this reach. Moreover, the air–water exchange also caused more α/γ -HCH and DDE to enter the surface water column, since all three compounds have relatively high Henry coefficients. Therefore, PC3 may provide information on the pathway (e.g. particles sedimentation) of the chemicals entering into river sediment system, which were then significantly influenced by the hydrodynamic conditions of the river.

The principal component scores of PC1 and PC2 for locations are also plotted in Fig. 8. Three main clusters can be found in this figure according with the classification of CA. In addition, it can be seen that all the sites downstream of the Shaying River are located in the areas with PC1 < 0 and PC2 < 0. Sites S6 and S7 were classified into cluster 3 with high loading for PC2 indicating the high concentration of phenolic EDCs in

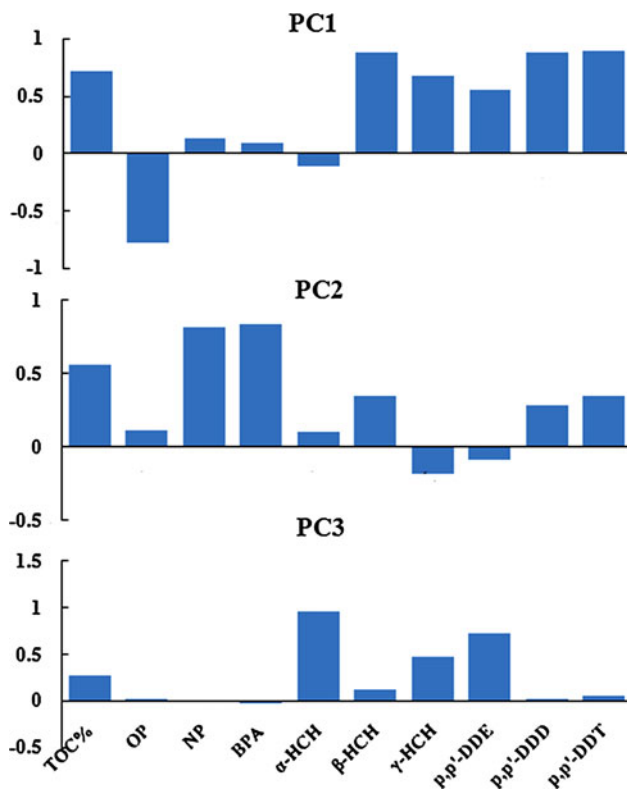


Fig. 7 Loadings of variables measured for the first three principal components

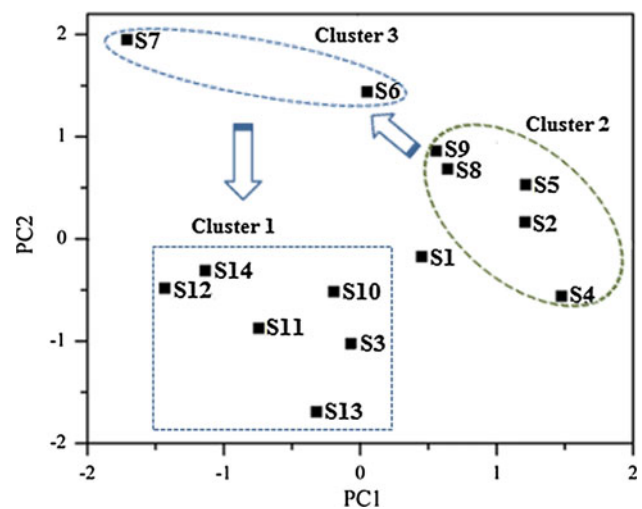


Fig. 8 Plot of sampling sites according to the scores in the first two principal components

Table 3 Classification function coefficients of discriminants analysis for three discriminant variables

Variables	Standard mode		
	Cluster 1	Cluster 2	Cluster 3
NP	0.103	0.222	0.258
<i>p,p'</i> -DDT	-0.036	0.072	-0.079
<i>p,p'</i> -DDD	0.642	1.468	1.601
Constant	-12.483	-70.916	-72.973

Fisher's linear discriminant functions

sediment. The arrow in the figure shows the flow direction of the Shaying River. Interestingly, site S9, which also falls into cluster 2, showed contamination characteristics similar to S8 due to the confluence of Jialu River and Ying River between S7 and S9 (Fig. 1).

Discriminant analysis was also carried out on raw data using stepwise modes in constructing discriminant functions to evaluate the spatial variation of the compounds. Two discriminant functions were found with Wilks' lambda values of 0.016 ($p < 0.001$) and 0.266 ($p = 0.001$), respectively. The total variance and canonical correlation coefficients were 85.3 % and 0.97 for function 1, and 14.7 % and 0.86 for function 2, respectively. The DA gave the good spatial classification for different sampling sites yielding an important data reduction with only three variables included (NP, DDD and DDT) for discriminating the classification, accounting for about 92.9 % correct assignments in spatial analysis (Table 3). Locations can be divided into three distinct groups using the stepwise method in DA and the classification is in accordance with that of cluster analysis.

Conclusions

The study firstly evaluated the levels, potential sources and behaviors of OCPs and phenolic EDCs in sediment of the Shaying River, the largest tributary of the Huaihe River in eastern China. OCPs and phenolic EDCs were detected in sediments of the whole river, most of them with concentrations higher than the sediment quality guidelines, thus indicating potential biological risks to aquatic organisms. Compositional characteristics showed that the HCHs in sediments could result from the use of both technical mixtures and lindane in the past, whereas the residues of DDT upstream partly come from the recent inputs revealed by the high content with respect to DDD and DDE. DDD prevails downstream, indicating a long-term anaerobic biodegradation in this reach. The spatial contaminant distribution upstream and downstream could have been influenced by the presence of a floodgate, which

significantly changed the flow regime of the river. In order to explore the driving factors determining the spatial distribution, multivariate statistical analysis was applied and the results showed that three distinct clusters can be obtained, mainly representing local pollution levels, biodegradation and hydrodynamic conditions. The DA also confirmed the classification of cluster analysis affording 92.9 % correct assignment in the spatial variation with only three discriminant variables: NP, DDD, and DDT. The results also showed that NP, DDD, and DDT could be considered the most important parameters for sediment quality assessment.

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