Distributions, sources, and ecological risks of DDT-related contaminants in water, suspended particulate matter, and sediments from Haihe Plain, Northern China

Yan Wang · Wei He · Ning Qin · Qi-Shuang He · Xiang-Zhen Kong · Shu Tao · Fu-Liu Xu

Abstract The residual levels of dichlorodiphenyltrichloroethane (DDT) and its metabolites (DDXs, including p,p′-DDT, DDD, and DDE) in water, suspended particulate matter (SPM), and sediments from major rivers, lakes, and reservoirs in Haihe Plain were measured with a gas chromatograph equipped with a ^{63}Ni microelectron capture detector. In the fall of 2004, the contents of the total DDXs in the water and SPM were 0.29 ± 0.69 ng L^{-1} and 423.13 ± 577.85 ng g^{-1} dry wt., respectively. In the spring of 2005, the total DDXs were 0.36 ± 0.91 ng L^{-1} for water and 35.93 ± 62.65 ng g^{-1} dry wt. for SPM. The average concentration of DDXs for sediments was 7.10 ± 7.57 ng g^{-1} dry wt. during the two seasons. The Eastern-Hebei-Province Coastland River System was the most polluted, which was mainly attributable to the extensive use of DDT pesticide and dicofol in that system. Recent DDT inputs still occur in some regions, as indicated by DDT/(DDD + DDE) > 1 at 29–36 % of the sites for water and 55–61 % of the sites for SPM. The potential ecological risks of DDT in the water were assessed using a species sensitivity distribution model. Only shrimp and crabs were found to have potentially affected fraction values of 1.63×10^{-3} to 2.27×10^{-4}, with probabilities beyond the hazardous concentration for 5 % of species (HC5) values of 1.90–2.56 %, suggesting only slight risks. DDXs in the sediments of some sites were also of potential risk to benthic organism based on consensus-based sediment quality guidelines.

Introduction

Dichlorodiphenyltrichloroethane (DDT) is a typical persistent organic pollutant that often bioaccumulates and has negative impacts on non-target organisms (Gao et al. 2008; Chau 2005). The intense use of DDT over the past several decades has caused increasing concerns globally. Although its production and usage have been globally regulated for years, there are still detectable levels of DDT and its metabolites (DDXs, including p,p′-DDT, DDD, and DDE) in various media worldwide (Pandit et al. 2006; Kurt-Karakus et al. 2006; Pinkney and McGowan 2006; Wong et al. 2005). In China, DDT was not officially banned for agricultural usage until 1983, and small-scale DDT application is still allowed for public health purposes. In addition, China is the second largest DDT manufacturer in the world, having produced over 0.4 million tons by the time it was banned, which accounts for 20 % of the world total production (Zhang et al. 2002; Wong et al. 2005).

Y. Wang · W. He · N. Qin · Q.-S. He · X.-Z. Kong · S. Tao · F.-L. Xu (✉)
MOE Laboratory for Earth Surface Process, College of Urban and Environmental Sciences, Peking University, Beijing 100871, China
e-mail: xufl@urban.pku.edu.cn

The Haihe Plain (114° E–120°E, 36° N–42°N) covers Beijing, Tianjin, and more than 20 other large and medium-sized cities in the provinces of Hebei and Shandong. This area has a population approximately 132 million people and has become one of the most developed areas in China. Nevertheless, this region has long suffered from severe water shortages, and dramatic water contamination has exacerbated the water scarcity by reducing the availability of usable fresh water (Yang et al. 2005a). Agriculture in this region is highly productive, leading to intensive application of agrochemicals, such as DDT, for many years (Gao et al. 2008). Moreover, large quantities of DDT and dicofol have been produced by several pesticide manufacturers in this area, with wastewater being discharged without effective treatment (Tao et al. 2007; Zhao et al. 2010).

To date, a few local studies of DDX contamination in water and sediments have been conducted in the Haihe Plain (e.g., in Beijing; Wang et al. 2003; Wan et al. 2005; Yang et al. 2005b; Chen et al. 2008; Sun et al. 2010; Zhao et al. 2010). However, these studies were limited by small spatial scales, limited sampling, and uneven distribution of sampling sites (Tao et al. 2008; Zhao et al. 2010). To determine the levels of contamination and ecological risks of DDXs in the entire Haihe Plain, it is necessary to conduct large-scale investigations. Although large-scale investigations on residual levels and distributions of DDXs in surface soils have been performed (Tao et al. 2008), there is little information on the residues, distributions, sources, and ecological risks of DDXs in the water-sediment system for the entire Haihe Plain. The primary objectives of the present study were to investigate the residual levels and temporal–spatial distributions of DDXs in the major rivers, lakes, and reservoirs in the water–sediment system of the Haihe Plain; identify their potential sources; and assess their potential ecological risks.

Materials and methods

Reagents and materials

A standard mixture stock of organochlorine pesticide (p,p′-DDT, p,p′-DDE, and p,p′-DDD), an internal standard, and a surrogate standard were purchased from AccuStandard (New Haven, CT, USA). A working

standard was prepared by diluting the stock solution in n-hexane. All solvents used for sample processing and analyses were HPLC grade. All glasswares were cleaned in an ultrasonic cleaner (KQ-500B, Kunshan Ultrasonic Instrument, Kunshan, China) and heated at 400°C for 6 h.

Sample collection and pretreatment

The distribution of the sampling sites included 17 rivers and 19 lakes and reservoirs, distributed among six river systems in the Haihe Plain, as shown in Fig. 1. Water, suspended particulate matter (SPM), and surface sediment samples were collected during October to November 2004 (fall) and during April to May 2005 (spring). The samples were collected according to the standard procedure proposed by Tao
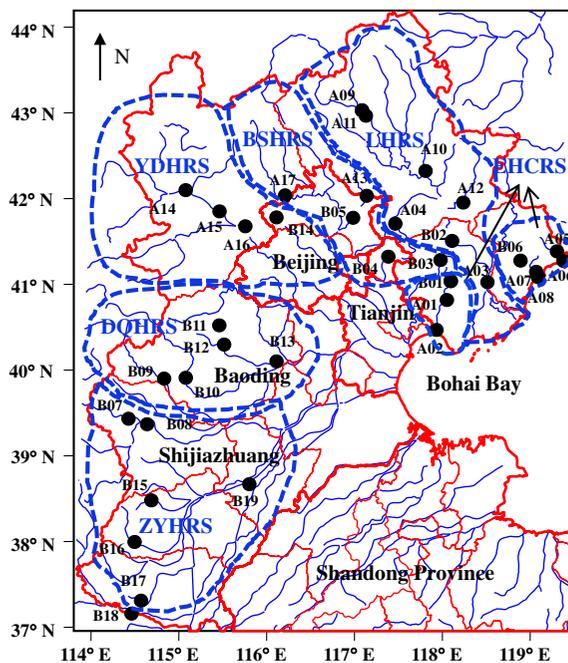

Fig. 1 Sampling area and location. *A* River samples; *B* lake and reservoir samples; *EHCRS* Eastern-Hebei-Province Coastland River System, including eight sample sites (A01, A02, A05, A06, A07, A08, B01, B06); *LHRS* Luan-He River System, including seven sample sites (A03, A04, A09, A10, A11, A12, B02); *BSHRS* Bei-San-He River System, including five sample sites (A13, A17, B03, B04, B05); *YDHRS* Yong-Ding-He River System, including four sample sites (A14, A15, A16, B14); *DQHRS* Da-Qing-He River System, including five sample sites (B09, B10, B11, B12, B13); *ZYHRS* Zi-Ya-He River System, including seven sample sites (A18, B07, B08, B15, B16, B17, B19)

et al. (2007). A global positioning system device was used to locate the sampling positions. Water samples were collected using pre-cleaned amber glass bottles. SPM samples were collected by filtering water samples through glass fiber filters (Sartorius, 0.47 μm, ashed at 450°C for 4 h) with a vacuum, wrapped them with aluminum foil, and then stored them in double-layered plastic bags. The surface sediment samples were collected using a grab sampler and pre-cleaned amber glass bottles. To reduce possible random variations, three sub-samples were collected for each sample at each site and then mixed thoroughly into a composite sample. All samples were stored at −18°C until analysis.

Sample extraction and cleanup

The sample extraction and cleanup were performed according to the procedure proposed by Tao et al. (2007) with some improvement. A solid-phase micro-extraction (SPME) device was purchased from Supelco Co. (Bellefonte, PA, USA) to extract the dissolved DDXs from the water samples. Commercially available 100-μm polydimethylsiloxane fibers housed in a manual SPME holder were used. The fibers were conditioned at 250°C for 2 h before use according to the manufacturer's recommendations, after which they were exposed to water samples in half-full 4-mL vials for a 30-min extraction. During extraction, the water samples were continuously agitated with a magnetic stir plate revolving at 1,000 rpm (Eyela RCH-3 D with 10×3 mm stirring bar, Japan). The SPME fiber tip was rinsed with double-distilled water and gently wrapped with a tissue to remove water and attached particles. The thermal desorption of the fiber occurred inside of the injection port for 4 min at 220°C, and once desorption was complete, the split vent was opened for the remainder of the chromatographic separation.

Both SPM and sediment samples were freeze-dried and weighed on an analytical balance. SPM samples were soxhlet-extracted for 48 h with DCM. Two grams of activated copper was added for desulfurization. The extracts were then concentrated to approximately 2–3 mL using a rotary evaporator; 10 mL of hexane was added, and the samples were concentrated to approximately 1 mL. The 1 mL extract was purified using a glass column packed with 12 cm SiO_2 (top) and 6 cm Al_2O_3 (bottom). The initial extracts eluted with 15 mL of hexane were discarded. The eluents containing

DDXs were then collected by eluting with 70 mL of a hexane–dichloromethane solution (2:5, v:v) and then concentrated to 1 mL by rotary evaporation and a gentle stream of purified N_2.

The sediment samples were ground and sieved through a 70-mesh sieve and then placed in an accelerated solvent extractor (ASE-300, Dionex, USA) equipped with 34 mL extraction cells. For extraction, 5 g of homogenized sediment sample was mixed with anhydrous sodium sulfate (1:5) and transferred into the extraction cell along with activated copper powder. The samples were extracted using hexane–dichloromethane solution (1:1, v:v) under 10,348 kPa at 125°C. The extraction was carried out twice in 1 cycle with 5 min of heating followed by 10 min of static extraction. The extracted solutions were concentrated to approximately 2 mL on a rotary evaporator at 35°C and then transferred onto the top of a glass column packed with 1 cm of anhydrous sodium sulfate, 1 g of activated Cu, 1 cm of anhydrous sodium sulfate, and 6 g of florisil. The elution procedure consisted of 50 ml hexane and 50 mL hexane–dichloromethane solution (7:3, v:v) at a rate of 2 mL min^{-1}. The eluate was collected and concentrated on the rotary evaporator and then rinsed three times with hexane. The final volume was reduced to 1 mL under a gentle stream of purified N_2.

Sample analysis and quality assurance

The samples were analyzed using an Agilent 6890 gas chromatograph equipped with a [63]Ni micro-electron capture detector and an HP-5 column (30 m × 0.25 mm inside diameter, 0.25 μm film thickness). The samples were injected using an auto-sampler at 50°C in splitless mode with a venting time of 0.75 min. The oven temperature was programmed to first increase from 50 to 150°C at 10°C min^{-1}, increase to 240°C at 3°C min^{-1}, and then maintain 240°C for 15 min. Nitrogen was used as both the carrier (1 mL min^{-1}) and makeup gas (60 mL min^{-1}). The injector and detector temperatures were 220°C. The details for the chromatographic method developed by our laboratory were described in the reference (Tao et al. 2007).

An external calibration procedure was used to quantify the extracted amount of target analytes from the SPME fibers, with a calibration ranging from 1–1,000 ng mL^{-1}. The Eqs. 1–3 are listed

below, where Area is the peak area and Amt is the concentration (nanograms per milliliter):

$$\text{For p, p}' - \text{DDE, Area} = 259.696 \times \text{Amt}, R^2 = 0.9993 \tag{1}$$

$$\text{For p, p}' - \text{DDD, Area} = 139.294 \times \text{Amt}, R^2 = 0.9990 \tag{2}$$

$$\text{For p, p}' - \text{DDT, Area} = 141.764 \times \text{Amt}, R^2 = 0.9994 \tag{3}$$

One-third of the samples were analyzed using spiked aqueous standard solution to determine the recovery and precision of the method. The average recoveries of p,p′-DDT, p,p′-DDD, and p,p′-DDE were 74, 80, and 75 % for water; 95, 97, and 89 % for SPM; and 85, 83, and 81 % for sediments, respectively. The limits of detection (LOD) for the target compounds were 0.1 ng L^{-1} for a 4 mL water sample, 2.4 ng g^{-1} for a 0.5 g SPM sample, and 0.24 ng g^{-1} for a 5 g sediment sample. Two procedural blank samples were analyzed to check for solvent and glassware contamination. All samples were extracted and analyzed in duplicate.

Other analyses

SPM content was determined by gravimetric analysis. A 1 L water sample was filtered through a pre-weighed glass fiber and then dried in a desiccator. The weight difference before and after filtration per unit volume of filtered water was defined as the SPM content (Gustafson and Dickhut 1997). The particulate organic carbon (POC) content in the SPM samples and the dissolved organic carbon (DOC) content in the water samples were determined using a total organic carbon (TOC) analyzer (TOC-5000A; Shimadzu Corp., Japan).

Results and discussion

Residual levels and distributions of DDXs in the water, SPM, and sediments

Residual levels of DDXs

DDXs were detected in 19 of 36 water samples in the fall of 2004 and 32 of 36 water samples in the spring of 2005; DDXs were detected in 100 % of SPM and sediment samples in both seasons. The residual levels of DDXs in the water, SPM, and sediments are tabulated in Table 1. For the water samples, the average total DDX (ΣDDXs) concentrations were 0.20±0.69 ng L^{-1} (fall) and 0.36±0.91 ng L^{-1} (spring). In the SPM, ΣDDXs were between 423.13±577.85 ng g^{-1} (fall) and 35.93± 62.65 ng g^{-1} (spring); the corresponding mean volume concentrations were 0.86±3.02 ng L^{-1} (fall) and 1.67± 2.71 ng L^{-1} (spring), which are almost five times higher than those in dissolved phase. The average content of ΣDDXs in the sediments was 7.10±7.57 ng g^{-1}. The ΣDDXs in the water, SPM, and sediments were log-normally distributed. The geometric means were 0.01 ng L^{-1} and 1.93 ng g^{-1} in the fall and 0.11 ng L^{-1} and 1.19 ng g^{-1} in the spring for water and SPM, respectively. For sediments, the geometric mean was 4.78 ng g^{-1}. Wilcoxon tests confirmed that there were significant differences in the ΣDDXs between seasons ($p < 0.001$) in the water and SPM. Positive relationships of ΣDDXs between the water and SPM, as well as between the SPM and sediments, were found in spring

Table 1 Mean residual levels of DDXs in water, SPM, and sediments from Haihe Plain

|	Water (ng L^{-1})		SPM (ng g^{-1}, dw)		Sediment (ng g^{-1}, dw)
	Fall 2004	Spring 2005	Fall 2004	Spring 2005	
DDE	0.02±0.03	0.09±0.18	78.50±129.02	8.29±13.03	1.81±2.23
DDD	0.06±0.21	0.14±0.53	102.18±152.94	12.57±41.35	2.65±5.29
DDT	0.16±0.52	0.13±0.26	242.44±348.37	15.06±18.93	2.63±1.67
Total DDXs	0.29±0.69	0.36±0.91	423.13±577.85	35.93±62.65	7.10±7.57

dw means dry weight

Fig. 2 Spatial distributions of total DDXs (ΣDDXs) in the ▶
water, SPM, and sediments from the six river systems in Haihe
Plain Means and standard deviations of ΣDDXs in water, SPM,
and sediments samples in six river systems. They are: Eastern-
Hebei-Province Coastland River System (*EHC*), Luan-He River
System (*LH*), Bei-San-He River System (*BSH*), Yong-Ding-He
River System (*YDH*), Da-Qing-He River System (*DQH*), Zi-Ya-
He River System (*ZYH*)

2005 (SPM Pearson relation coefficient, 0.654 ($n=28$,
$p<0.001$); sediment Pearson relation coefficient, 0.598
($n=18$, $p=0.009$)).

Compared with other investigations in China,
the mean ΣDDXs levels in the water from the
Haihe Plain (<LOD–5.09 ng L^{-1}) were similar to
those in the Wuhan section of the Yangtze River
(0–16.71 ng L^{-1}) (Tang et al. 2008), Gaobeidian Lake
(0.17–14.4 ng L^{-1}) (Li et al. 2008), and Guanting Res-
ervoir (3.10 ng L^{-1}) (Wang et al. 2003) but lower than
those in the Qiantang River (0.80–97.54 ng L^{-1}) (Zhou
et al. 2006), Taihu Lake (200–9,300 ng L^{-1}) (Feng et al.
2003), and the Tonghui River (18.79–663.3 ng L^{-1})
(Zhang et al. 2004). For the SPM samples, the residual
levels of ΣDDXs (0.12–1,830.25 ng g^{-1}) in the Haihe
Plain were comparable to those in Tianjin (2,690 ng g^{-1})
(Tao et al. 2007) but were considerably higher than
those in the Wuhan section of the Yangtze River
(0.46–2.72 ng g^{-1}) (Tang et al. 2008) and Deep Bay
(0.1–10.0 ng g^{-1}) (Qiu et al. 2009). The levels of
ΣDDXs in the sediments in the Haihe Plain (0.28–
37.44 ng g^{-1}) were substantially higher than those in
the Tonghui River (0.11–3.78 ng g^{-1}) (Zhang et al.
2004), comparable to those of the Minjiang River
(1.57–13.06 ng g^{-1}) (Zhang et al. 2003) and the Huaihe
River (4.07–23.89 ng g^{-1}) (Sun et al. 2010), and lower
than that observed in the Pearl River Delta (3–
163 ng g^{-1}) (Chau 2005). These comparisons indicate
that the water and sediments in the Haihe Plain were
moderately polluted by DDXs, while the SPM was
severely polluted by DDXs.

Spatial distributions of ΣDDXs

The spatial distributions of ΣDDXs in the water, SPM,
and sediments in the six Haihe Plain river systems
during fall 2004 and spring 2005 are shown in
Fig. 2. In the water, ΣDDXs in all six river systems
had higher concentrations in spring 2005 than in fall
2004, except for the LHRS and ZYHRS. For the
LHRS, pollution was more severe in the fall 2004
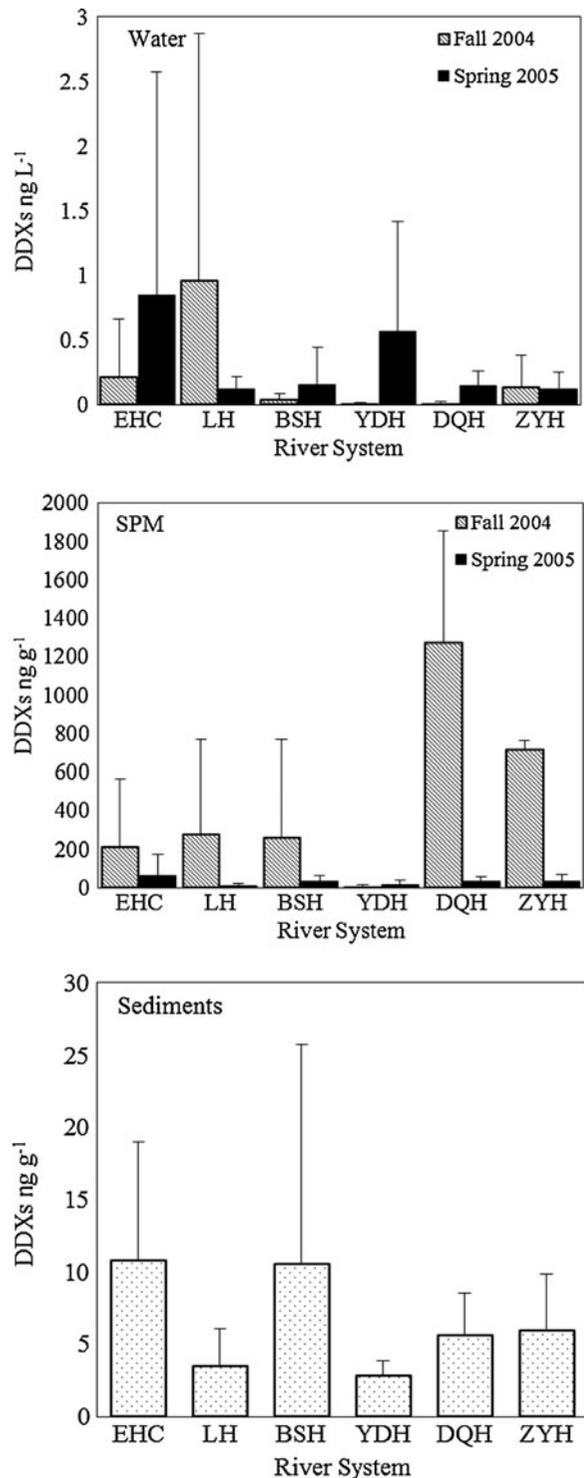
primarily due to the extreme case at site A12, which
greatly increased the mean ΣDDXs concentration. If

this high value was removed, there was an increase in the ΣDDXs concentrations in the spring as with the other systems. For the ZYHRS, DDXs were found in the similar residual levels during both seasons. The ΣDDXs pollution in the BSHRS and DQHRS was slight in both seasons, whereas the ΣDDXs concentration in YDHRS significantly rose in the spring. Heavy pollution was found in both fall and spring in the EHCRS, especially at site A6, where high ΣDDXs values were detected (1.27 ng L^{-1} in the fall of 2004 and 5.09 ng L^{-1} in the spring of 2005).

As seen from Fig. 2b, in the fall of 2004, the descending order for the average contents of ΣDDXs in the SPM was DQHRS >ZYHRS >LHRS > BSHRS >EHCRS >YDHRS. However, in the spring of 2005, the mean ΣDDXs concentrations decreased, and the order was EHCRS >ZYHRS >DQHRS > BSHRS >YDHRS >LHRS. In contrast with the ΣDDXs residue in the water, concentrations in the SPM were considerably higher in the fall of 2004 than in the spring of 2005, except for YDHRS, where the ΣDDXs residual levels were much lower than other river systems in both seasons, and the spring ΣDDXs levels were slightly higher.

Pecipitation is considered to be one of the main factors that influence the distribution of pollutants in water because it has a direct dilution effect on the pollutant concentration in the dissolved phase. However, organochlorine contaminant concentrations and loads in the particulate phase are related to the origin and abundance of suspended solids and are not highly influenced by water flow (Gomez-Gutierrez et al. 2006; Doong et al. 2008). In the Haihe Plain, summer (June–September) precipitation contributes approximately 80 % of the annual rainfall (Wang et al. 2010). Thus, the water level in the fall of 2004 might have been higher than that in the spring of 2005. This could explain the seasonal distribution of ΣDDXs, with higher concentrations in the spring of 2005, in accordance with results found in the Pearl River in southern China (Yang et al. 2004).

To explain the spatial distribution of ΣDDXs, the pollution status of each river system needs to be considered. Historically, there was extensive water pollution in the Haihe Plain (Wang et al. 2010). ZYHRS is one of the most polluted rivers in the Hebei Province because it received wastewater from the Shijiazhuang, Xingtai, Handan, and Hengshui areas. The major pollution source of DQHRS is Baoding City, which houses two urban

chemical plants. In addition, Tangshan City is an important agricultural base in the Hebei Province, and
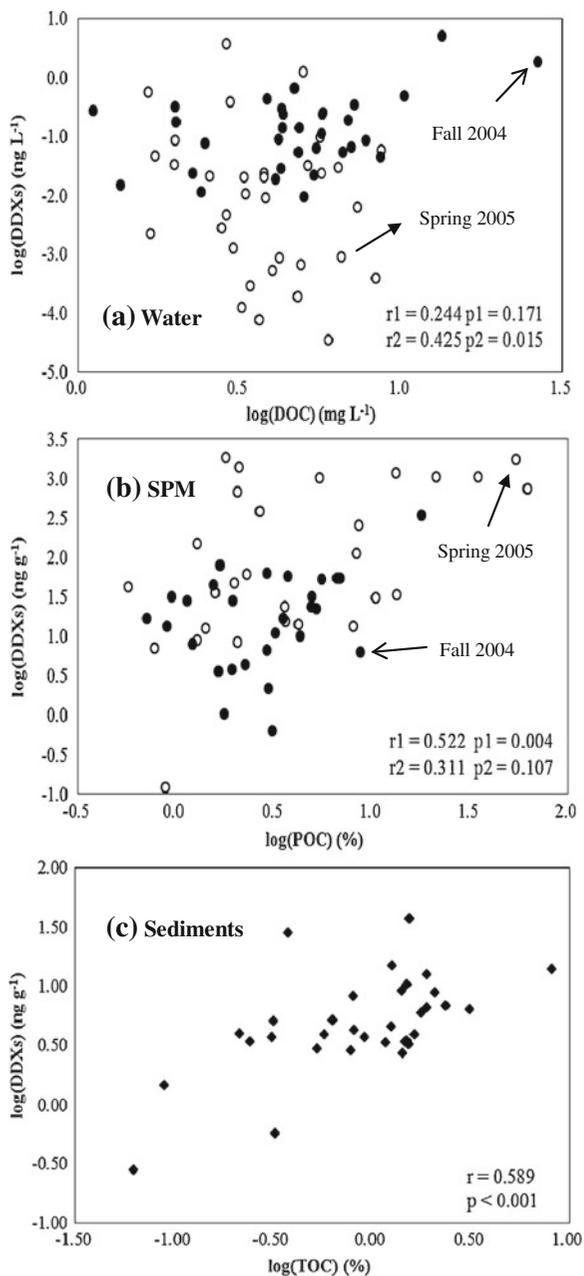

Fig. 3 Relationships between the log-transformed DDXs and organic carbon contents in a water, b SPM, and c sediments from Haihe Plain. All data were log-transformed. r value represents correlation coefficient and p value represents significance. For water and SPM, the *filled symbols* and *number 1* represent data in fall 2004, while the *blank symbols* and *number 2* are data in spring 2005. For sediments, *symbols* represent data with average values of both seasons

Qinghuangdao City has a developed shipbuilding industry. Both Tangshan and Qinghuangdao are located in the EHCRS, and the application of pesticides and antifouling paint used on ships are potential DDXs sources. Moreover, it should be noted that there were often large standard deviations in the concentrations of DDXs among different sampling sites within the same river system. River dilution and the point-source pollution might help to explain some of these deviations in the DDXs distributions. For instance, in both fall and spring, the DDXs content in the water and SPM were higher upstream than downstream in the Douhe River, which may have resulted from a sewage plant and ongoing canal construction upstream (Wan et al. 2005).

Analyses of water and suspended matter provide information relevant to short-term temporal variations in the river, while data from the surface sediments may represent a historical overview of river pollution (Wu et al. 1999). In this study, the descending order for the ΣDDXs in the sediments was EHCRS ~ BSHRS > ZYHRS > DQHRS > LHRS > YDHRS, which confirmed that the pollution in YDHRS was limited. As with other river systems, although SPM and sediments should come from the same origin due to sedimentation and resuspension, it is clear that SPM was more easily influenced by occasional pollution.

Relationships between organic carbon and DDXs in water, SPM, and sediments

The relationships between DDXs and organic carbon content in the water, SPM, and sediments are shown in Fig. 3. The correlations between log-transformed DDXs and DOC content in the water were significant in the spring of 2005 ($r=0.487$, $n=28$, $p<0.01$) but not significant in the fall of 2004 ($r=-0.374$, $n=17$, $p>0.05$) (Fig. 3a), which might suggest that the relationship between DDXs and DOC content in the water was only relevant in highly contaminated situations (Tan et al. 2009). On the contrary, the log-transformed DDXs and POC contents in the SPM were significantly correlated in both the fall of 2004 ($r=0.456$, $n=28$, $p<0.05$) and the spring of 2005 ($r=0.449$, $n=28$, $p<0.05$) (Fig. 3b). However, these relationships were not linear, as indicated by the decentralized distribution of the data (Fig. 3a, b). This may be attributed to factors that influence DDXs residues, such as historic usage and physicochemical properties (Yang et al. 2005a, b). In addition, with increasing levels of organic condensation, the nonlinear phenomena of adsorption and competitive adsorption were more prominent (Xing and Pignatello 1998). For sediments, the TOC content is supposed to be an essential factor for DDXs residues. In this study, a positive correlation between the log-transformed DDXs and TOC content in the sediments was demonstrated ($r=0.589$, $n=33$, $p<0.001$) (Fig. 3c). Similar correlations between hydrophobic pollutants and organic matter content have been reported in many other cases (Pinkney and McGowan 2006; Yang et al. 2005a, b).

Composition and possible sources of DDXs in water, SPM, and sediments

Compositions of DDXs in water, SPM, and sediments

The composition of DDXs in three phases is plotted in Fig. 4. In the fall of 2004, DDT was the primary

Fig. 4 Percentage compositions of DDXs in water, SPM, and sediments from Haihe Plain. Percentages of every DDX component in water and SPM in fall 2004 and spring 2005, respectively. For sediments, the percentages were the average of both seasons. The *dotted parts* represent DDT, the *slash parts* represent DDD, and the *black parts* represent DDE
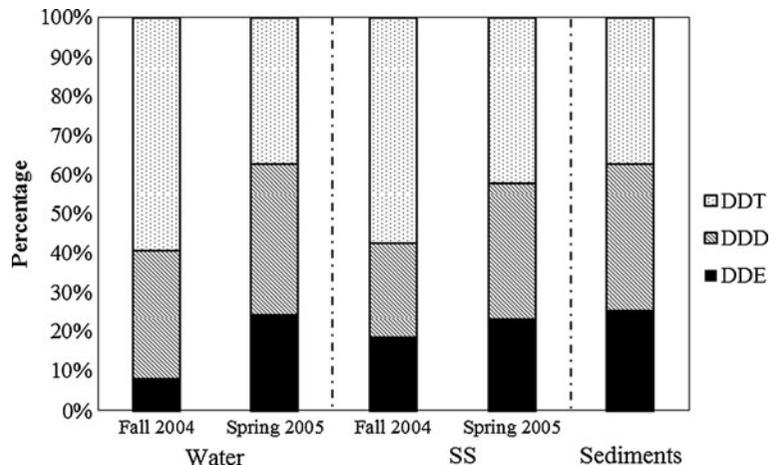
component of the water, with an average percentage of 59.19 % of total DDXs, followed by DDD (0.001–98.18 %; mean, 32.62 %) and DDE (0.81–99.99 %; mean, 8.19 %). In the spring of 2005, the average percentages for DDT, DDD, and DDE were 37.20 % (2.36–89.99 %), 38.17 % (0.23–59.01 %), and 24.63 % (0.78–97.40 %), respectively, showing an increase in the contributions of degradation products. In the SPM, DDT accounted for the most abundant fraction of total DDXs in both seasons, but its percentage decreased from 57.30 % (3.68–81.13 %) in the fall of 2004 to 41.93 % (10.32–92.90 %) in the spring of 2005, corresponding to increases of 24.15 % (11.31–54.66 %) to 34.99 % (2.88–66.21 %) for DDD, and 18.55 % (1.58–84.39 %) to 23.09 % (2.24–77.65 %) for DDE. The occurrences of DDXs in the sediments were as follows: DDD (13.35–75.46 %; mean, 37.39 %) ~ DDT (7.31–78.71 %; mean, 37.06 %) > DDE (2.87–58.60 %; mean, 25.54 %). Variations in the relative content of the parent DDT compound and its degradation products could provide useful information on their sources.

Possible sources of DDXs

DDXs sources can be identified from their compositions. The portion of DDT degradation products (DDD and DDE) indicates whether they result form new inputs or historical usage because DDT can be degraded gradually to DDD and DDE. If the DDT/(DDD + DDE) ratio is greater than 1, it indicates that there is a new input of DDT in a given sample, whereas if this ratio is not greater than 1, the DDT is due to historical inputs (Hitch and Day 1992). A DDD/DDE > 1 implies that DDD is the main degradation product, which is indicative of anaerobic degradation conditions, whereas a DDD/DDE < 1 indicates that DDE is the main degradation product, which is indicative of aerobic degradation conditions (Hitch and Day 1992).

To visualize the above analysis, a triangle diagram, with DDE, DDT, and DDD as the *X, Y,* and *Z* axes, respectively, is presented in Fig. 5. The triangular diagram can be divided into three areas, A, B, and C, for the DDT, DDD, and DDE, respectively. The DDT/(DDD + DDE) > 1 of area A indicates new DDT input, whereas DDT/(DDD + DDE) < 1 in areas B and C imply historical DDT usage. Furthermore, anaerobic

conditions with DDD as a main degradation product are indicated in area B (DDD/DDE > 1), while aerobic conditions with DDE as a main degradation product are indicated in area C (DDD/DDE < 1) (Hitch and Day 1992). The triangle diagrams for DDXs in the water, SPM, and sediments from each sampling site in the Haihe Plain are presented in Fig. 5.

Figure 6 illustrates that in the area A (DDT/(DDD + DDE) > 1), there were 9 water and 17 SPM sampling sites in the fall of 2004, and 13 water and 18 SPM sampling sites in the spring of 2005. In the fall of 2004, 9 out of the 31 water sites were distributed mainly in the LHRS, DQHRS, and ZYHRS, whereas 17 out of 28 SPM sites were distributed throughout the six river systems. In the spring of 2005, 13 out of 36 water sites and 17 out of 28 SPM sites were distributed among all of the studied six river systems, respectively. This suggests that there might be new DDT inputs at 29–36 % of the water sites and 55–61 % of the SPM sites, and that the DDT pollution in spring was heavier than that in fall. This is in accordance with studies on DDT in rainwater from Beijing (Xu et al. 2009). The new DDT inputs in some areas of the Haihe Plain were also identified by other more local studies, including DDXs residues in human milk (Yu et al. 2003), pine needles (Xu et al. 2004), air particulates (Xu et al. 2005), soil (Shi et al. 2005; Li et al. 2008), water (Chen et al. 2008), and rainfall (Xu et al. 2009). The illegal use of DDT pesticide associated with extensive agricultural activities, as well as the use of dicofol for shipbuilding paints, is likely the primary contributor of these high DDT residual levels. These new DDT inputs can enter the water system through soil erosion, and dry and wet precipitations.

The residual levels of DDX pollution in water and SPM were more sensitive to recent changes, while sediment concentrations reflect historical pollution. In the sediments of the Haihe Plain, the proportion of parent DDT overwhelmed its metabolites at 18 of 33 sampling sites, indicating that sediment DDXs had suffered significant degradation in less than half of the sites. The 18 sites in area A included all LHRS sites, most of the YDHRS, DQHRS, and ZYHRS sites, but only three sites in BSHRS and EHCRS, suggesting that there had been a recent DDT input in LHRS, YDHRS, DQHRS, and ZYHRS.

Fig. 5 *Triangle* diagrams for DDXs compositions in **a** water, **b** ▶
SPM, and **c** sediments at each sampling site from Haihe Plain.
Compositions of DDXs and the metabolic conditions of DDT.
The *X*, *Y*, and *Z* axes of the triangular diagram represent DDE,
DDT, and DDD percentages, respectively. The triangular dia-
gram can be divided into three areas, A, B, and C. In area A, the
DDT/(DDD + DDE) ratio is >1; in area B, the ratio of DDD/
DDE >1; in area C, DDD/DDE <1. For water and SPM, the
filled stars represent data in fall 2004 and the *blank dots* repre-
sent data in spring 2005. For sediments, the *blank triangles*
represent data with average values of both seasons

The sites in areas B and C of Fig. 6 with DDT/
(DDD + DDE) < 1 suggest historical DDT usage.
DDE dominated the degradation products in water at
most of the sites, which was consistent with a previous
study (Zhou et al. 2008). However, there was no
obvious predominance of DDE or DDD in the SPM
and the sediments, which was likely attributed to
different redox conditions at each site, as well as
multiple sources for the SPM.

Potential ecological risks of DDXs in the water
and sediment

Potential ecological risks of DDXs in the sediments

There is currently no uniform standard for risk assess-
ment of OCPs in sediments. In the present study, the
ecological risks of DDXs in sediments were compared
to the consensus-based sediment quality guidelines
(CB-SQGs), which were developed by assembling
published SQGs. According to their original narrative
intent, these SQGs were classified into two categories
and then used to develop two consensus-based SQGs
for each contaminant: threshold effect concentrations
(TEC; below which adverse effects are not expected)
and probable effect concentrations (PEC; above which
adverse effects are expected more often than not)
(MacDonald et al. 2000). Table 2 presents the CB-
SQG values of DDX and ∑DDXs. In this study, the
DDD concentrations exceeded the TEC at sites A06
and B04, with the latter also exceeding the PEC value,
indicating potential risks. There were seven sites that
exceeded the TEC for DDE and four sites that
exceeded the TEC for DDT but were all below the
PEC. Of the sites above the TECs of DDX, most were
from EHCRS, with only three located in BSHRS,
DQHRS, and ZYHRS. Mean concentrations of ∑DDXs
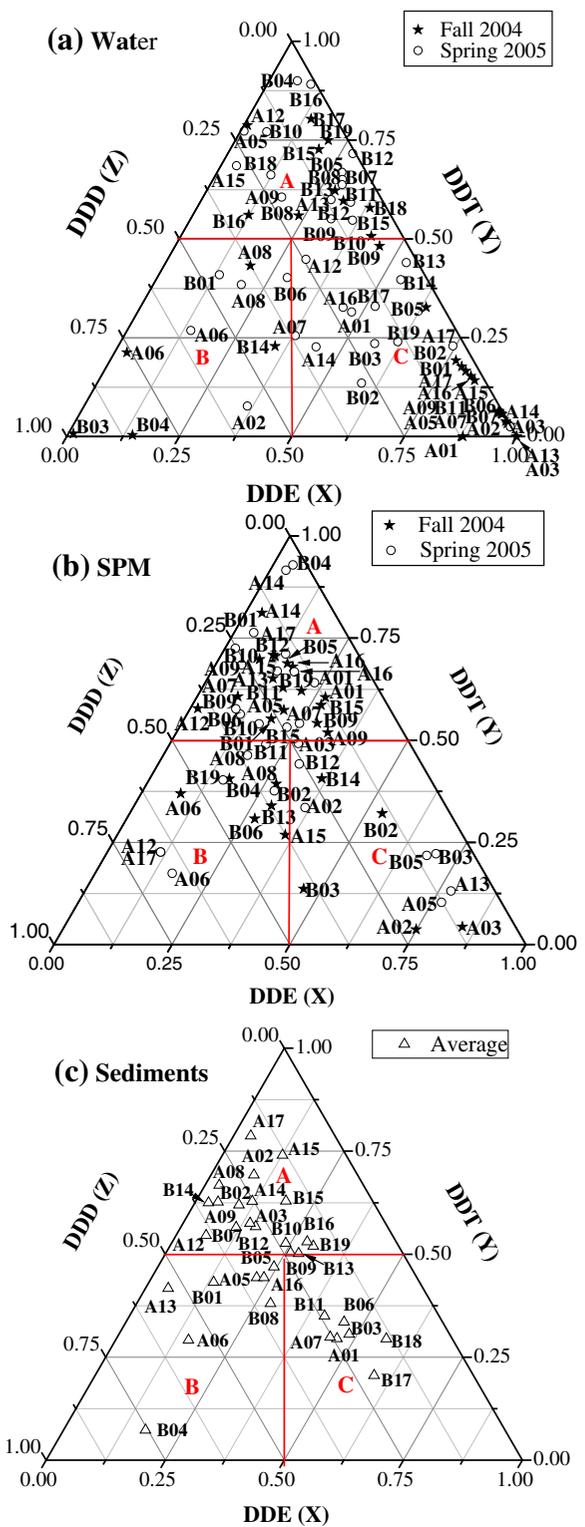
between TEC and PEC were found at 13 of 33
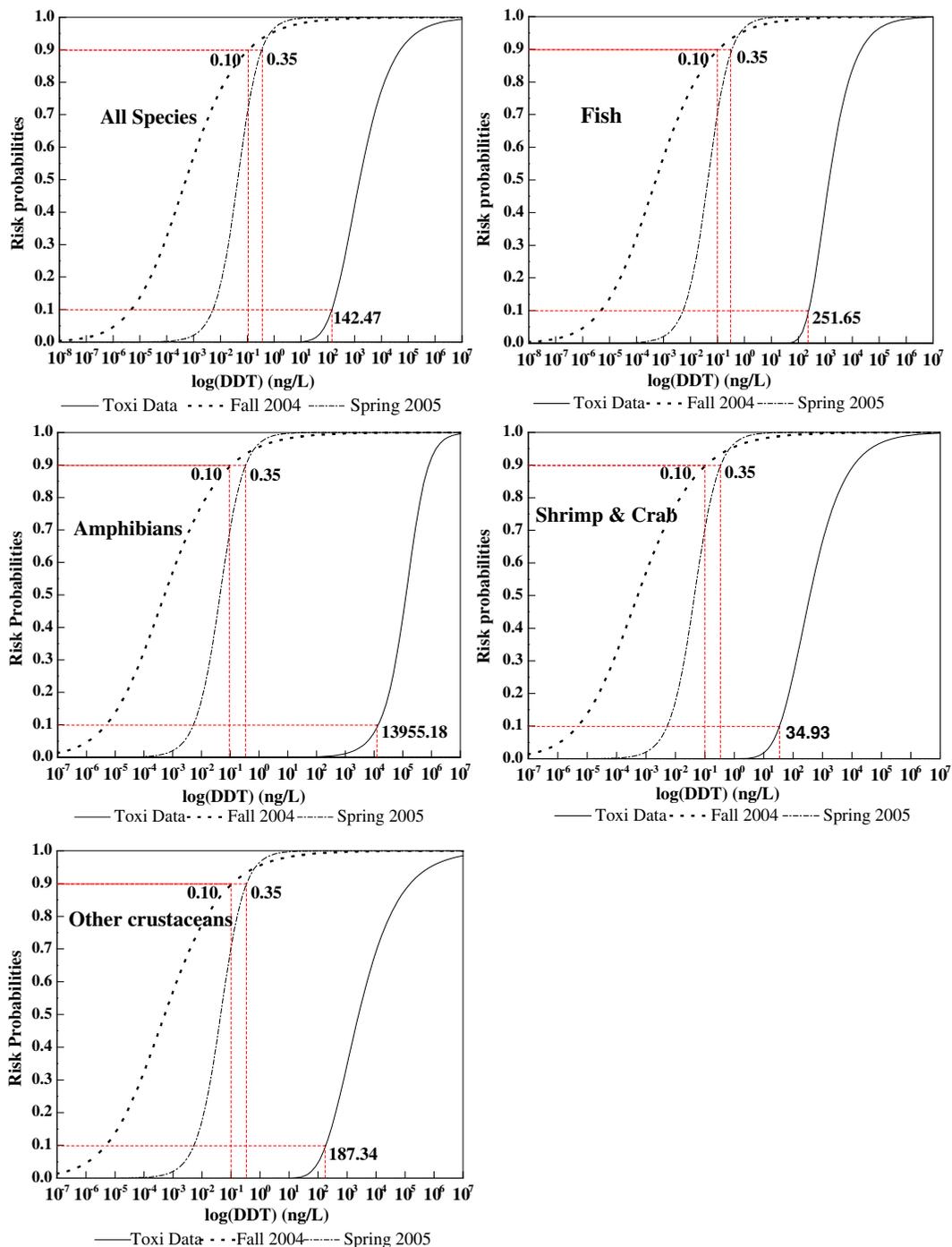sampling sites, across all six river systems except

Fig. 6 Cumulative distribution curves of DDT toxicity values and its exposure levels in the water form Haihe Plain. The *x* axis of a cumulative distribution curve represents log transformed DDT concentration, while the *y* axis represents the risk probabilities. The area below the curve is the ecological risk for the specific species. The *full lines* in figures represent toxicity values, which were calculated by toxic data from database and are only related to species; the *dot lines* and *dash dot lines* represent exposure values in fall 2004 and spring 2005, respectively, both of which were calculated by the exposure levels of p,p′-DDT in Haihe Plain. The margin of safety (MOS10) was calculated by dividing the 10th percentile for SSD of ecotoxicity data by the 90th percentile for the cumulative distribution of exposure data

Table 2 Potential ecological risks of DDX in sediments from Haihe Plain based on CB-SQGs

DDXs	TECs (ng g^{-1}, dw)[a]	PECs (ng g^{-1}, dw)[b]	This study (ng g^{-1}, dw)	TEC-PEC (%)	≥PEC (%)
DDD	4.88	28	1.81	0.03	0.03
DDE	3.16	31.3	2.65	0.21	0
DDT	4.16	62.9	2.63	0.12	0
∑DDXs	5.28	572	7.10	0.39	0

[a] TEC (threshold-effect concentration)

[b] PEC (probable-effect concentration)

YDHRS. Based on these results, it was concluded that DDXs were of possible concern and adverse biological effects in the Haihe Plain.

Potential ecological risks of DDXs in water

A species sensitivity distribution (SSD) model was applied to evaluate the ecological risks of p,p′-DDT to different species. An SSD describes the cumulative distribution of the eco-toxicity and exposure data (Posthuma et al. 2002; Wang et al. 2009). The toxicity data were collected from the EPA ECOTOX database (http://cfpub.epa.gov/ecotox/). The search criteria included the type of freshwater body, LC50 endpoints, exposure duration of less than 10 days, and laboratory tests. The species considered in the SSD were algae, fishes, amphibians, shrimps and crabs, and other small crustaceans. The BurrliOZ tool (designed by Australia's Commonwealth Scientific and Industrial Research Organization (CSIRO 2008)) was employed to calculate the relevant SSD parameters (Table 3). The potentially affected fraction (PAF), a measure of the toxic risk probability of pollutants, can be obtained using the BurrIII (Eq. 4), ReWeibull (Eq. 5), or Repareto

(Eq. 6) equations, where x is the pollutant concentration (micrograms per liter) and b, c, and k are parameters.

$$\mathrm{PAF}(x) = 1 / \left[1 + (b/x)^c\right]^k \tag{4}$$

$$\mathrm{PAF}(x) = \exp(-b/x^c) \tag{5}$$

$$\mathrm{PAF}(x) = (x/b)^k \tag{6}$$

The PAFs for different species are tabulated in Table 4. In the fall of 2004, the ecological risks of p,p′-DDT for fish and small crustaceans were very low with PAF values of near 0, while the ecological risk probabilities for other species were higher. Specifically, the PAF for amphibians was 1.07×10^{-10} – 9.05×10^{-5}, and for shrimp and crab, it was 9.83×10^{-29} – 1.63×10^{-3}. The PAF values for all species varied from 1.97×10^{-34} to 2.79×10^{-5}. The situation was similar in the spring of 2005, but slightly higher ecological risks for each species were found; the PAF values for all species were between 3.05×10^{-18} and 2.03×10^{-6}.

Table 3 SSD parameters of p,p′-DDT calculated by Burrliz O

Species	Curve type	Parameter and its value		
		b	c	k
All species	BurrIII	21.00	0.55	7.69
Algae	Repareto	1.00×10^7		0.72
Fishes	ReWeibull	102.23	0.69	
Amphibians	BurrIII	2.19×10^5	1.32	0.63
Shrimp and crab	BurrIII	7.10	0.56	6.67
Other crustaceans	ReWeibull	25.44	0.46	

Table 4 PAF, MOS10, and probability beyond HC5 for DDT in water from Haihe Plain

		PAF[a]		MOS10[a]	Probability beyond HC5[a]
		Max value	Min value		
All species	Fall	1.97×10^{-34}	2.79×10^{-5}	1,375.23	1.41 %
	Spring	3.05×10^{-18}	2.03×10^{-6}	411.44	0.39 %
Fish	Fall	~0	1.73×10^{-21}	2,429.08	0.84 %
	Spring	~0	1.47×10^{-36}	726.74	0.09 %
Amphibian	Fall	1.07×10^{-10}	9.05×10^{-5}	134,706.33	0.02 %
	Spring	1.65×10^{-7}	4.69×10^{-5}	40,301.78	<0.01 %
Shirmp and crab	Fall	9.83×10^{-29}	1.63×10^{-3}	337.14	2.56 %
	Spring	1.91×10^{-14}	2.27×10^{-4}	100.87	1.90 %
Other crustaceans	Fall	~0	2.21×10^{-7}	1,808.38	1.71 %
	Spring	1.44×10^{-218}	2.64×10^{-10}	541.03	0.67 %

[a] PAF, MOS10, and HC5 represent the potentially affected fraction, the margin of safety, and the concentration when 95 % of species are protected in an ecosystem, respectively

Because there was a range for PAF for each species, which was difficult to compare, the margin of safety (MOS10) from the SSD model was used to illustrate the ecological risk of contaminants to aquatic organisms in the Haihe Plain (Zolezzi et al. 2005). This was calculated by dividing the 10th percentile for the SSD of eco-toxicity data by the 90th percentile for the cumulative distribution of exposure data. Based on the cumulative distribution curves of DDT exposure level and eco-toxicity data (Fig. 6), the MOS10 values for different species could be calculated (Table 4). In both fall and spring, the MOS10 values of p,p′-DDT for each species were above 1, indicating that p,p′-DDT posed little potential ecological risk to these species, particularly for amphibians, which had MOS10 orders of magnitude ranging from 4 to 5. This indicates that the risk to this group could be neglected (Table 4).
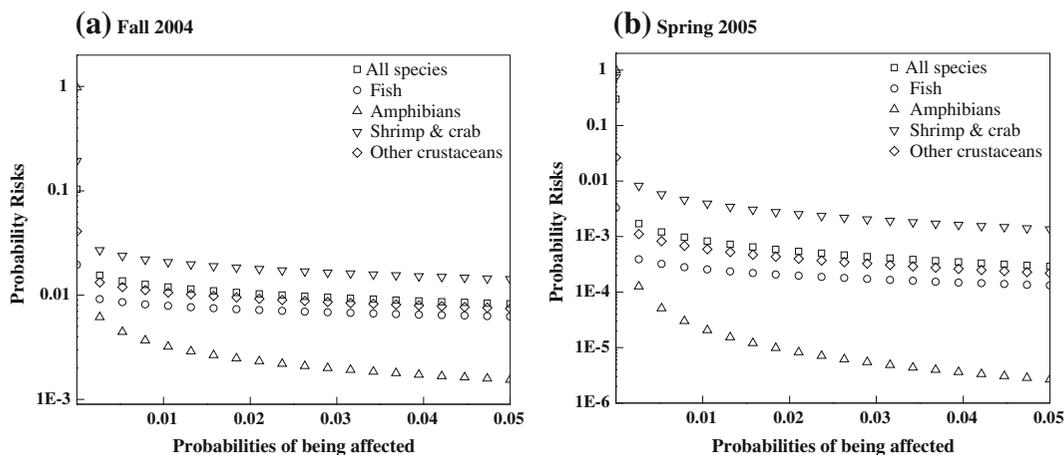

Fig. 7 Joint probability curves of DDT exposure values and ecotoxicological values in water from Haihe Plain. The x axis of a joint probability curve represents the probability of being affected for specific species, while the y axis represents the probability risks. HC5 represents the concentration when 95 % of species are protected in an ecosystem. When HC5 is chosen as the acceptable concentration for ecological risks, the probability risks of p,p′-DDT beyond HC5 for specific species can be found on the joint probability curve

The concentration of 5 % of cumulative probability in an SSD curve (HC5) can also be used to evaluate ecological risk. HC5 represents the concentration when 95 % of species are protected in an ecosystem (Wang et al. 2008). According to the joint probability curve of DDT exposure levels and ecological toxicity values, when HC5 was chosen as the acceptable concentration for ecological risks, the probability risks of p,p′-DDT beyond HC5 could be calculated. The results are presented in Table 4 and Fig. 7. The position of the curve in Fig. 7 reflects the ecological risk of species; the closer the curve is to the X axis, the lower the risk. Figure 7 and Table 4 revealed that the ecological risks of p,p′-DDT were highest for shrimps and crabs, followed by small crustaceans and fishes, and finally amphibians. The probabilities beyond HC5 for shrimps and crabs were 2.56 % in the fall and 1.90 % in the spring.

Conclusion

The highest DDX concentrations and detectable frequencies were found in the SPM, followed by the sediments and then the water. The content of total DDXs in the water was higher in the spring than in the fall; the opposite was true for the SPM. The EHCRS was the most polluted river system, most likely due to extensive agriculture activities and shipbuilding industry in this area. The DDX compositions in the water, SPM, and sediments revealed that recent DDT inputs still occur in some areas of the Haihe Plain. The potential risks for benthic organisms at some sites were found based on CB-SQGs. There were slight ecological risks of DDT in the water to shrimps and crabs.

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