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Tiered probabilistic assessment of organohalogen compounds in the Han River and Danjiangkou Reservoir, central China

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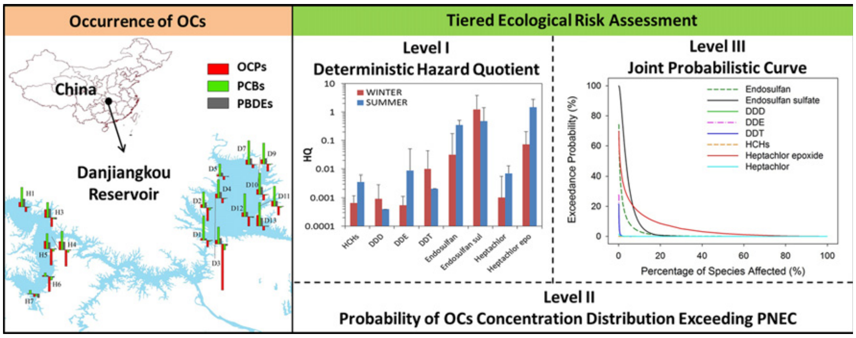
HIGHLIGHTS

- The first report on OCPs, PCBs and PBDEs in Danjiangkou Reservoir
- Ecological risk of the chemicals was assessed by tiered probabilistic method.
- Human health risk through water consumption was investigated.

GRAPHICAL ABSTRACT



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ABSTRACT

Occurrence of organohalogen contaminants (OCs) including 12 organochlorine pesticides (OCPs), 7 polychlorinated biphenyl congeners (PCBs) and 7 polybrominated diphenyl ethers (PBDEs) were investigated in the Han River, which is the largest tributary of the Yangtze River, and Danjiangkou Reservoir, the source of water for China's South-to-North Water Diversion Project. OCPs were found to be dominant in water, with concentrations of 0.14–11 and 2.9–59 ng L^{-1}during winter and summer, respectively. In sediment, OCPs were also predominant contaminants during summer (5.0–1.7 × 10^2 ng g^{-1}), whereas during winter PCBs (4.3–2.3 × 10^2 ng g^{-1}) were dominant. Concentrations of OCs observed during this study were generally less or comparable to those from other locations in the world. Concentrations of OCPs were significantly greater in lower reaches of the Han River, during winter. This observation might be due to proximity of this location to more developed areas. Distributions of OCs between water and sediment were not at steady state except for PBDEs during winter. This disequilibrium is likely due to continuing inputs of pollutants. A tiered assessment of risks to aquatic organisms was conducted for OCs. Initially species sensitivity distributions (SSD) were employed to determine predicted no effect concentration (PNEC), followed by evaluation based on hazard quotients (HQ). In subsequent tiers, a probabilistic approach was used to develop joint probability distributions, where species sensitivity distributions were compared to distributions of measured concentrations of OCs. Consistent results were obtained by use of all methods, which suggested endosulfans and heptachlors could pose risk to local aquatic organisms. Furthermore, heptachlors and PCBs might also cause potential adverse effect to health of humans through consumption of water.

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1. Introduction

Persistent Organic Pollutants (POPs) are hydrophobic, toxic, persistent, bioaccumulative and globally transportable (Gao et al., 2016; Loganathan, 2012; Loganathan, 2016). The *Stockholm Convention*, of which the People's Republic of China is a signatory, is a global treaty that was developed to protect human health and the environment from POPs (UNEP, 2009). Twenty nine chemicals or classes of chemicals are currently included on the list (http://chm.pops.int/). These chemicals are either banned or have their use restricted or are scheduled for global, virtual elimination. Among the first 12 compounds added to the *Stockholm Convention* were organohalogenated contaminants (OCs) such as organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs). Subsequently polybrominated diphenyl ethers (PBDEs) were added to the list. OCPs, such as DDTs and HCHs were widely used, during the last century, in agriculture for control of pests. PCBs were formerly used widely as dielectric fluids in transformers, flame retardants and plasticizers. PBDEs have also been used as flame retardants in textile, vehicles and furniture (Sun et al., 2016). Despite the ban or restrictions on uses of the above chemicals, they have been detected in various environmental compartments such as water, air and soils globally (Everaert et al., 2015; Ge et al., 2013; Jiang et al., 2010; Koh et al., 2015; Whitehead et al., 2015), and still need to be considered in policy decisions and in some cases dealt with to avoid adverse effects on humans or the environment.

Danjiangkou Reservoir (DJKR, 32°36′-33°48′N, 110°59′-111°49′E) is located at the confluence of the Dan (Ch: *Danjiang*; DJ) and Han (Ch: *Hanjiang*; HJ) Rivers, which together form the largest tributary of the Yangtze River, China. DJKR is now designed as the source of water for the Middle Route Project (MRP), which is part of the South-to-North Water Diversion Project (SNWDP) of China. This project will bring 9.5–13 billion tons of water from the DJKR to North China and mitigate shortages of water in Beijing, Tianjin, Henan and Hebei provinces, with total area of 155,000 km^2 including >20 cities and a population of 198 million people covered (http://www.nsbd.gov.cn/). Therefore, it was deemed crucial to ensure the quality of water from the DJKR. Currently available data in this catchment include turbidity, dissolved oxygen, chemical oxygen demand (COD), biological oxygen demand (BOD) (Li et al., 2009), trace elements, metals (Li et al., 2008), nutrients (Liu et al., 2012), and polycyclic aromatic hydrocarbons (PAHs) (Bu et al., 2014). However, to our knowledge, little information on OCs was available and few reports have been published. Therefore, occurrence, distribution and risks posed by OCs in this region are far from well understood, which might be of great concern for drinking water security of the vast population in central and northern China, especially when taking into account persistence and potential for bioaccumulation of these chemicals, which might pose threats to aquatic species and human health even at trace environmental concentrations. Considering sources of water to the DJKR is mainly from the upper HJ, which flows through 6 provinces in western and central China, it was deemed essential to investigate occurrence and risk of OCs in the HJ, along with that of the DJKR.

Comparison of point estimates of measured environmental concentrations with toxicant reference values to express hazard quotients (HQs), is widely adopted in risk assessments of toxicants, because of its simplicity and efficacy. However, this method is quite conservative and only suitable for preliminary screening-level risk assessment (Bartell, 1996) and it is unable to describe probabilities of effects of a defined magnitude. Alternatively, probabilistic risk assessments can quantify distributions and probabilities of hazard so that risks can be estimated. For instance, the joint probability curve (JPC) method developed by comparing distributions of measured exposure concentrations and toxicity effects (species sensitivity distributions, SSDs) can describe the likelihood of exposure exceeding various thresholds of effect (Solomon et al., 2000). To get more credible results for management of risks posed by exposure to chemicals, use of tiered approaches from point estimates to probabilistic methods is considered to be a better choice (Zolezzi et al., 2005). More detailed information for the higher tiers of the assessment is progressed to only if the lower tiers indicate the potential for adverse effects.

Major objectives of this study were to: (1) elucidate occurrence of OCs in the DJKR and HJ, including concentrations, profiles of relative proportions of congeners, as well as spatial and temporal distributions; (2) assess distributions of OCs between water and sediment, and where appropriate, natural and anthropogenic sources of OCs; (3) assess risks posed by OCs to humans and aquatic organisms in the DJKR and HJ region. Results of this work will be useful for assessing safety of drinking water of central and northern China residents, as well as for managers of the DJKR, HJ and SNWDP of China.

2. Methods and materials

2.1. Chemicals and materials

Chemicals considered in this study included 12 OCPs, 7 indicator PCB congeners defined by GEMS (Global Environmental Monitoring System)/Food (WHO Regional Office for Europe, 2004), as well as the 7 PBDEs of primary interest identified by the USEPA Method 1614 (USEPA, 2007). Detailed information about the standards and other chemicals, such as internal standard pentachloronitrobenzene (PCNB), surrogate standard PCB-209, as well as materials used for extraction, are available in the Supplementary materials.

2.2. Sampling

Samples of water and sediments were collected in November 2014 and June 2015. These two periods were chosen to represent dry and wet seasons, respectively. Locations on the HJ and DJKR from which samples were collected are shown (Fig. 1). Along the HJ, locations were on 14 main tributaries (T) and below their confluence with the main stream (M). For DJKR, locations were distributed evenly along the reservoir, with 7 sites on the HJ portion (Han Reservoir, H) and 13 sites in Dan River part (Dan Reservoir, D). For HJ, both water and sediment were collected. Water was collected using high-density polyethylene bottles, which were pre-cleaned and rinsed with water from the location of sampling prior to use. Sediments were collected using a stainless steel grabber. Samples were transported to the laboratory soon after collection, where water was filtered through 0.45 and 0.22 μm membranes sequentially before extraction, and sediments were freeze dried, homogenized and stored at −20 °C until extraction.

2.3. Extraction and identification and quantification of OCs

Water and sediments were extracted by use, with minor modification, of previously reported methods (Sun et al., 2016; Yang et al., 2015). More details can be found in the Supplementary materials. Target chemicals were quantified using an Agilent 7890A gas chromatograph (GC) equipped with an electron capture detector (μECD) and a Model 5975 mass spectrometer (MS), where the MS was operated in scan mode for identification and μECD signals were acquired for quantification. Detailed operating conditions of the instrumental analysis are available in the Supplementary materials document. Total organic carbon (TOC) (%) of sediments and dissolved organic carbon (DOC) concentration (mg L^{-1}) in water were analyzed by use of a TOC analyzer (Elementar, Germany).

2.4. Quality assurance and quality control (QA/QC)

Recoveries of analytes throughout extraction and injection were monitored by use of both solvent and matrix spikes. Two levels of spiking of 26 target analytes were conducted: 10 and 20 ng. For OCs in both water and sediment, recoveries were 60–120%. The surrogate PCB-209

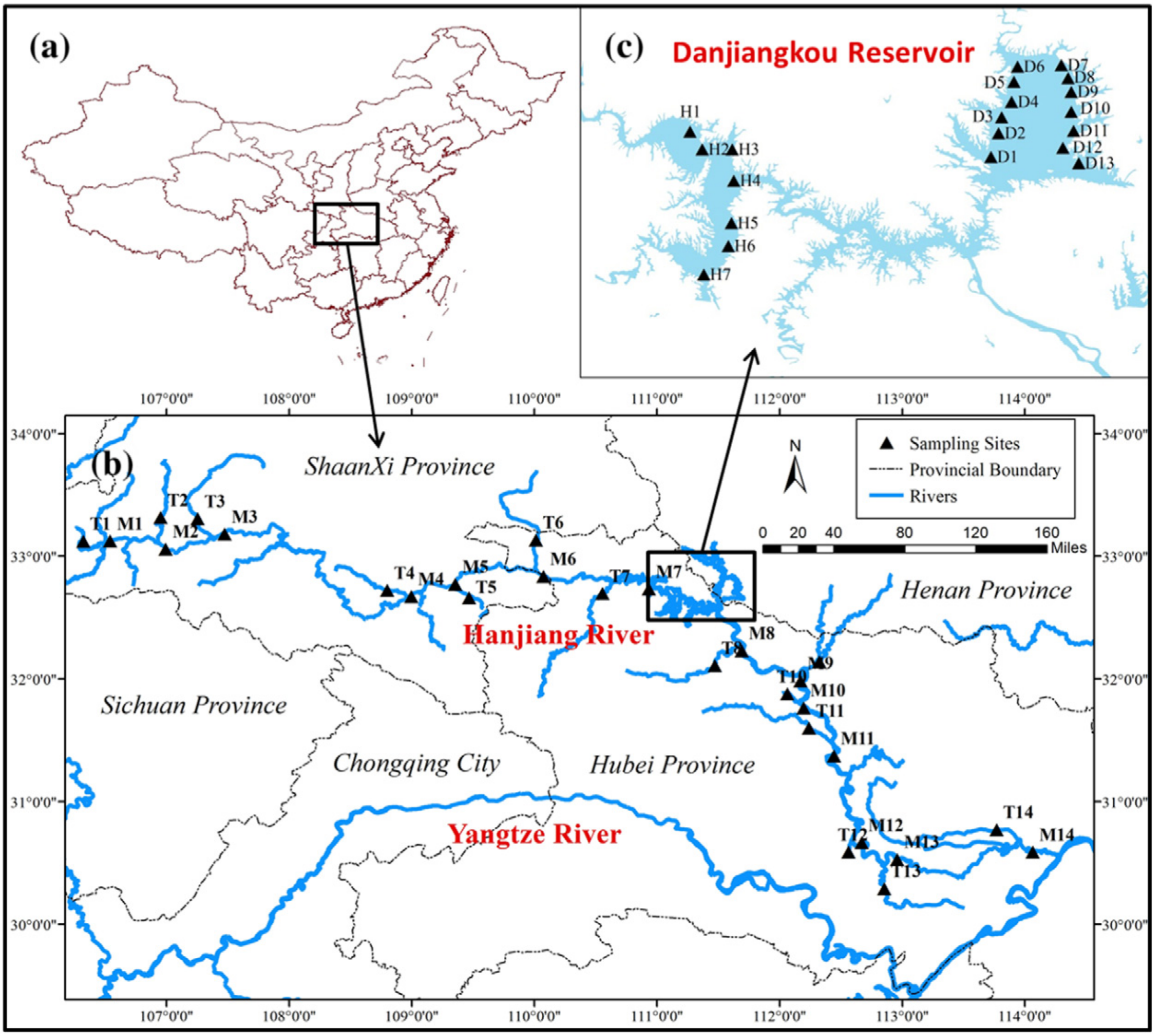

Fig. 1. Locations of sampling sites on the Han River (HJ) and Danjiangkou Reservoir (DJKR).

was added to every sample before extraction to "mimic behaviors of the target analytes throughout sample preparation and instrument determination", and "assess matrix effects as well as verify proper processing and instrument performance for each sample" (USEPA Method SW-846). To normalize the fluctuation of instrumental responses, known amounts of the internal standard pentachloronitrobenzene (PCNB) were added just before injection. Calibration curves containing at least 5 points were established for quantification, and coefficients of determination (r^2) were >0.99. Limits of detection (LOD), defined as concentrations of analytes that generated peak heights of 3 times the noise for OCs in water and sediment samples were in the range of 0.01–0.5 ng L^{-1} and 0.001–0.05 ng g^{-1} dw, respectively. Degradation of DDT in the inlet of the gas chromatograph was <15%, the maximum limit suggested by USEPA Method 8081B. Concentrations of OCs were not corrected for recoveries of surrogate standard.

2.5. Assessment of risks

The ecological risk assessment (ERA) was performed in a tiered manner (Jin et al., 2012), as categorized by the USEPA Ecological Committee on FIFRA Risk Assessment (ECOFRAM, 1999). Level I: this is based on deterministic quotients of point values of exposure and effect. The effect values were derived from the species sensitivity distributions (SSD) recommended by the European Commission (EC, 2003). The median lethal concentration (LC50) or median effect concentrations (EC50) for each toxicant were collected from the ECOTOX Database (http://cfpub.epa.gov/ecotox/) and published literature. The screening and quality assessment of the toxicity values were based on the following principles: Freshwater species of plants and single-celled animals were discarded; Local species distributed in China were preferred; Exposure duration was 2–4 days; Values of the same species that were 2 orders of magnitude different from other studies were removed; Geometric mean values were calculated as the species mean acute values (SMAVs) for SSD simulation if more than one toxicity data available for the same species. The final, selected toxicity data for SSD were listed as Table S3 in the Supplementary materials. LC50 or EC50 values were divided by an Acute to Chronic Ratio (ACR) to yield a chronic value. Although ACRs varied from 1 to 18,000, the ACR of 25 was applied because the mean value was 25 or less for 93% of chemicals (Wang et al., 2009). SSDs were generated by fitting cumulative probability distributions of logarithmically transformed, predicted chronic data as a function of rank-assigned centile, by use of the BurrliOZ program (Version 2.0, Commonwealth Scientific and Industrial Research Organization, Australia). The hazardous concentration to affect 5% of species (HC5) with 50% confidence interval was calculated from the SSD. This was selected to protect 95% of species (Liu et al., 2016). Predicted No Effect Concentration (PNEC) was derived by dividing the HC5 by an application factor (AF) of 1–5 (EC, 2003). Considering the amount of supporting evidence for SSD such as the use of non-native species and multi-species values, an application factor (AF) of 5 was preferred, especially for OCs such as endosulfan sulfate and heptachlor epoxide. The hazard quotient (HQ) was calculated by normalizing the measured environmental concentration of OCs (exposure) with corresponding Predicted No Effect Concentrations (PNECs) (effect). Level II: this level was a semi-probabilistic approach, performed by comparing distribution of concentrations of OCs measured in environmental media (exposure) with a fixed value of effect (PNEC). Probabilities of exposure exceeding the specific effect levels were determined. Potential affected fractions (PAF) of species at a certain concentration of OCs (geometric mean and maximum values of measured concentrations, representing common and worst cases respectively) were also evaluated. Level III: this was carried out by use of joint probability curves (JPCs) based on probability distributions of concentrations in water (exposure) and response (SSD). The Probabilistic Risk Assessment Tool (PRAT) developed by K.R. Solomon, J.P. Giesy and P.D. Jones (Solomon et al., 2000) was employed for simulation of JPC. JPCs describe probabilities (*y*-axis) that the measured environmental concentrations exceed the specific level associated with a particular magnitude or probability of effect. For example, the proportion of species affected (*x*-axis of the JPC). The closer the JPC is to the axes, the lesser the probability of hazardous effects (Jin et al., 2014).

Risks to health of humans caused by the OCs were assessed based on the method recommended by the USEPA (1989), where the carcinogenic risk as well as the non-cancer risk (represented by the hazardous index, HI) were assessed according to the oral slope factor (SF) and the chronic reference dose (RfD). The detailed procedures of the assessment can be found in the Supplementary materials.

2.6. Statistical analysis

Statistical analyses were performed by use of SPSS software (IBM, USA) and Microsoft Excel 2000. Normality was confirmed by the Shapiro-Wilk test, and Kruskal-Wallis test on ranks was performed when normality test failed. Two-tailed *t*-tests were performed for comparison of concentrations of OCs between the two seasons. One-way ANOVA tests followed by pairwise multiple comparison procedures using Dunn's method was performed to investigate whether the concentrations of OCs varied significantly between spatial sectors. Pearson correlation analysis was performed to check the linear relationship between TOC, DOC and OCs concentrations. A p-value < 0.05 was considered statistically significant.

3. Results and discussion

3.1. Profiles of OCs

3.1.1. In water

Concentrations of 12 OCPs in water from the Han River and DJKR ranged from 0.14 to 11 ng L^{-1} and from 2.9 to 59 ng L^{-1}, with mean concentrations of 2.2 and 19 ng L^{-1} during winter and summer, respectively (Table 1). Most frequently detected OCPs were HCHs, which occurred in >90% sites during both seasons. DDTs were generally not detected in samples from most sites, whereas frequencies of detection of both heptachlors and endosulfans were greater during summer. Especially, heptachlor-epoxide was detected in 96% sites with a mean concentration of 15 ng L^{-1} during summer. This might be related to historical or current uses of heptachlor and chlordane in this area for agricultural pest and termite control. Heptachlor-epoxide is a major degradation product of heptachlor by soil microbe through epoxidation (Lichtenstein et al., 1970; Miles et al., 1969) and by photo-oxidation

Table 1

Concentrations of OCs in water from the Han River (HJ) and Danjiangkou Reservoir (DJKR), ng L^{-1}. Heptachlor-e means heptachlor epoxide, and endosulfan-s represents endosulfan sulfate. ΣOCPs, ΣPCBs and ΣPBDEs represent the total concentrations of 12 OCPs, 7 PCBs and 7 PBDEs, respectively.

	Winter				Summer			
	Mean	Min	Max	Det. freq.	Mean	Min	Max	Det. freq.
α-HCH	0.10	0.01	0.37	100%	1.1	0.33	8.3	100%
β-HCH	0.11	<LOD	1.3	92%	0.33	0.20	2.5	100%
γ-HCH	0.05	0.01	0.27	100%	0.40	0.38	0.67	100%
δ-HCH	0.25	0.04	1.3	100%	0.88	0.60	1.8	100%
heptachlor	0.10	<LOD	3.3	50%	0.72	0.50	4.2	100%
heptachlor-e	0.72	<LOD	3.9	35%	15	<LOD	55	96%
α-endosulfan	0.08	<LOD	2.6	52%	0.70	0.50	2.1	100%
p, *p*′-DDE	0.01	<LOD	0.02	31%	0.09	<LOD	2.7	21%
β-endosulfan	0.01	<LOD	0.05	2%	0.19	0.14	0.53	100%
p, *p*′-DDD	0.01	<LOD	0.08	8%	<LOD	<LOD	<LOD	0%
endosulfan-s	0.74	<LOD	11	81%	0.29	0.17	3.8	100%
p, *p*′-DDT	0.07	<LOD	1.5	13%	<LOD	<LOD	<LOD	0%
ΣOCPs	2.2	0.14	11		19	2.9	59	
PCB28	0.21	0.10	0.52	100%	0.62	<LOD	11	31%
PCB52	0.17	<LOD	8.1	2%	1.1	<LOD	9.2	27%
PCB101	0.06	0.04	0.27	100%	0.10	<LOD	1.1	19%
PCB118	0.13	0.10	0.70	100%	0.01	<LOD	0.24	4%
PCB138	0.14	0.10	0.75	100%	0.13	<LOD	5.8	8%
PCB153	0.12	0.10	0.23	100%	0.07	<LOD	1.1	13%
PCB180	0.14	0.10	1.8	100%	0.07	0.03	0.33	100%
ΣPCBs	0.97	0.55	9.0		2.1	0.04	12	
BDE28	0.22	0.20	0.45	100%	0.16	0.15	0.43	100%
BDE47	0.37	0.13	0.73	100%	0.35	0.05	4.5	100%
BDE99	0.18	0.15	0.29	100%	0.05	0.03	0.12	100%
BDE100	0.29	0.21	0.54	100%	0.13	0.10	0.20	100%
BDE153	0.19	0.17	0.28	100%	0.08	<LOD	0.54	79%
BDE154	0.18	0.15	0.88	100%	0.01	<LOD	0.09	77%
BDE183	0.16	0.15	0.21	100%	<LOD	<LOD	<LOD	0%
ΣPBDEs	1.6	1.3	2.3		0.78	0.35	5.0	

Table 2

Concentrations of OCs in sediment samples from Han River (HJ) and Danjiangkou Reservoir (DJKR), ng g^{-1} dw. Heptachlor-e means heptachlor epoxide, and endosulfan-s represents endosulfan sulfate. ΣOCPs, ΣPCBs and ΣPBDEs represent the total concentrations of 12 OCPs, 7 PCBs and 7 PBDEs, respectively.

	Winter				Summer			
	Mean	Min	Max	Det. freq.	Mean	Min	Max	Det. freq.
α-HCH	0.03	0.01	0.08	100%	0.45	0.33	1.1	100%
β-HCH	1.0	<LOD	4.5	95%	5.3	0.20	48	100%
γ-HCH	3.3	0.01	9.2	100%	0.42	0.38	0.94	100%
δ-HCH	0.48	0.00	1.1	100%	1.2	0.50	4.8	100%
heptachlor	0.40	0.07	3.1	100%	20	0.64	1.1×10^2	100%
heptachlor-e	0.20	<LOD	0.43	91%	0.58	0.15	2.1	100%
α-endosulfan	0.27	0.01	0.74	100%	0.22	0.17	0.52	100%
p, *p*′-DDE	0.39	0.01	2.6	100%	1.2	0.30	7.2	100%
β-endosulfan	0.62	0.02	2.0	100%	0.52	0.33	1.7	100%
p, *p*′-DDD	0.35	<LOD	2.1	98%	0.24	0.17	0.96	100%
endosulfan-s	0.39	0.13	3.6	100%	0.88	0.67	1.8	100%
p, *p*′-DDT	0.81	0.17	2.0	100%	1.4	1.00	10	100%
ΣOCPs	8.2	0.67	20		32	5.0	1.7×10^2	
PCB28	4.0	0.63	24	100%	0.13	<LOD	0.74	85%
PCB52	12	0.40	1.6×10^2	100%	2.4	<LOD	16	98%
PCB101	7.4	0.50	47	100%	1.3	<LOD	8.2	98%
PCB118	6.9	0.56	24	100%	0.15	<LOD	2.6	61%
PCB138	3.0	0.63	13	100%	0.24	<LOD	1.4	76%
PCB153	4.6	0.70	30	100%	0.76	<LOD	2.3	93%
PCB180	1.5	0.80	3.0	100%	0.16	<LOD	3.6	63%
ΣPCBs	40	4.3	2.3×10^2		5.0	<LOD	26	
BDE28	1.6	0.09	7.1	100%	0.16	<LOD	2.2	80%
BDE47	4.7	0.09	7.6	100%	0.19	<LOD	3.6	78%
BDE99	0.17	0.03	0.92	100%	0.19	<LOD	1.3	78%
BDE100	1.0	0.10	3.8	100%	0.06	<LOD	0.19	59%
BDE153	1.6	0.13	3.5	100%	0.08	<LOD	0.64	61%
BDE154	0.27	0.05	2.4	100%	0.06	<LOD	0.52	52%
BDE183	0.16	0.08	1.1	100%	0.43	<LOD	5.3	70%
ΣPBDEs	9.5	0.67	21		1.2	<LOD	6.8	

(Buser and Mueller, 1993). In addition, technical chlordane used as a pesticide is a complex mixture of chemicals including heptachlor (Buchert et al., 1989; Buser and Mueller, 1993; Saha and Lee, 1969). Relative proportions of OCPs are shown (Fig. S1). Heptachlors and endosulfans each accounted for 37% of the total concentration of OCPs during winter, while in summer, the proportion of OCPs contributed by heptachlors was 79%. Total concentrations of the seven indicator PCB congeners in water were 0.55–9.0 and 0.04–12 ng L^{-1} during winter and summer, respectively. During summer concentrations of PCBs were greater than those during winter ($p = 0.026$, t-test). Total concentrations of PBDEs were 1.3–2.3 and 0.35–5.0 ng L^{-1} in winter and summer, respectively, with most congeners detected frequently except BDE183, which was not detected in summer.

Compared with results of other studies (Table S1), dissolved concentrations of OCPs observed in the present work were less than those measured in water from the Qiantang River (7.68–269.4 ng L^{-1}) (Zhou et al., 2006) and Chao Lake (1.6–1678.6 ng L^{-1}) (Liu et al., 2013), but comparable with those observed in India (3.17–49.13 ng L^{-1}) (Pandit et al., 2006). Concentrations of PCBs were less than those reported for other investigations in China, including Baiyangdian Lake (19.46–131.62 ng L^{-1}), Tonghui River (31.58–344.9 ng L^{-1}) (Dai et al., 2011; Zhang et al., 2004), but greater than Venice Lagoon in Italy (0.25–0.792 ng L^{-1}) (Matteo et al., 2005), and comparable with Houston Ship Channel of Texas (0.49–12.49 ng L^{-1}) (Howell et al., 2008) or Seine Estuary of France (2.0–21.2 ng L^{-1}) (Cailleaud et al., 2007). PBDEs were less than those in Pearl River Estuary (26.1–156.9 ng L^{-1}) (Luo et al., 2008), comparable with Tai Lake (1.2 ± 1.7 ng L^{-1}) (Qiu et al., 2010) and Lake Shihwa of Korea (0.16–11.0 ng L^{-1}) (Moon et al., 2012), but greater than those in Hong Kong (0.0311–0.1187 ng L^{-1}) (Wurl et al., 2006).

3.1.2. Sediments

Total concentrations of OCPs in sediments were 0.67–20 and 5.0–1.7×10^2 ng g^{-1} dw during winter and summer (Table 2). All targeted OCPs were detected in >90% of samples. The most abundant OCs were γ-HCH and heptachlor, during winter and summer, respectively. HCHs accounted for 58% of total concentrations of OCPs in sediment during winter, followed by DDTs (19%), endosulfans (16%) and heptachlors (7%) (Fig. S1). However, in summer the dominant group was heptachlors (63%), followed by HCHs (23%), DDTs (9%) and endosulfans (5%). Total concentrations of PCBs ranged from 4.3 to 2.3×10^2 and from <LOD to 26 ng g^{-1} during winter and summer, respectively. All PCB congeners were detected in 100% of samples during winter, whereas in summer frequencies of detections were less. Tri-CB and tetra-CB were the major PCB congeners detected in water, whereas in sediments the most abundant congeners were tetra- and penta-CB (Fig. S2a). Total

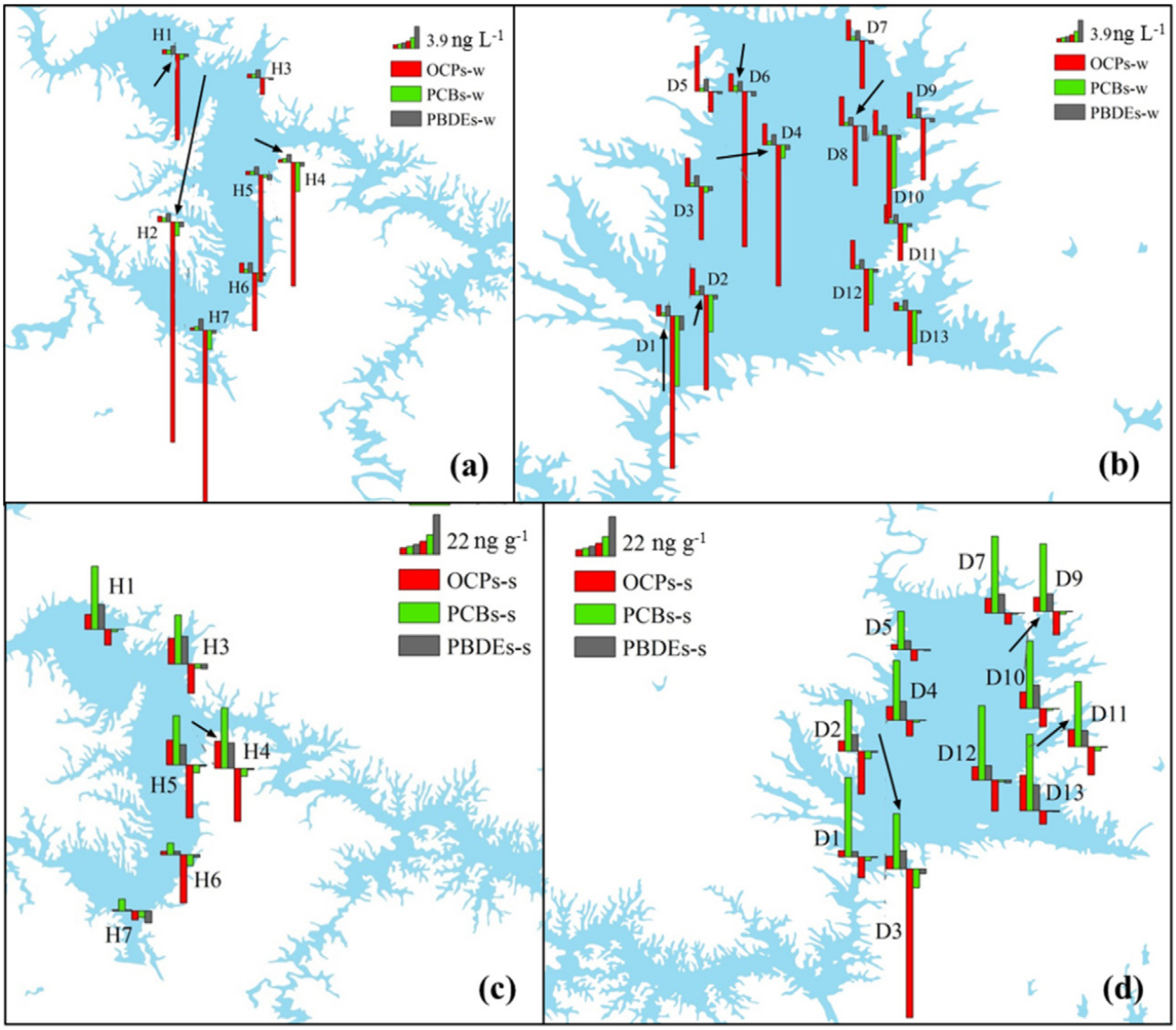

Fig. 2. Spatial and temporal distribution of OCs in the Danjiangkou Reservoir, (a) in water from Han Reservoir, (b) in water from Dan Reservoir, (c) in sediment from Han Reservoir and (d) in sediment from Dan Reservoir. The upward columns represent concentrations of OCs in winter, and the downward columns represent OCs concentrations in summer.

concentrations of 7 PBDEs were 0.67–21 and <LOD-6.8 ng g^{-1} dw, during and summer, respectively. BDE-47 was the dominant congener during winter. The pattern of homolog dominance was: tetra- > penta- > tri- ≈ hexa- > hepta-, with sediment collected during summer as an exception, where hepta-BDE was dominant (Fig. S2b).

Compared with other sites around the world (Table S2), OCPs in sediments collected during this work were less than those in the Pearl River Delta (10.05–447.13 ng g^{-1} dw) and Qiantang River of China (23.11–316.5 ng g^{-1} dw) (Sun et al., 2014; Zhou et al., 2006), comparable with Chao lake of China (0.9–36.9 ng g^{-1} dw) (Liu et al., 2013) and Mumbai coastline of India (4.3–25.8 ng g^{-1} dw) (Pandit et al., 2006). For PCBs, the concentrations during winter were greater than Hugli Estuary of India (0.18–2.33 ng g^{-1} dw) (Guzzella et al., 2005) and Mekong River Delta of Vietnam (0.039–9.2 ng g^{-1} dw) (Minh et al., 2007), and less than Hai River of China (0.177–253 ng g^{-1} dw). Concentrations of PBDEs were comparable with most reports available, such as in Hong Kong (1.7–52.1 ng g^{-1} dw) and the Pearl River Delta of China (0.04–94.7 ng g^{-1} dw) (Liu et al., 2005; Mai et al., 2005), Masan Bay of Korea (1.3–19 ng g^{-1} dw) (Hong et al., 2010) and Scheldt River of The Netherlands (0.6–17.6 ng g^{-1} dw) (de Boer et al., 2003).

3.2. Spatial and temporal distribution of OCs

In the Han River, the distribution of OCs in water (Fig. S3) and sediment (Fig. S4) are shown against the sampling map, in order to illustrate the spatial and temporal patterns. For most of the sites, OCPs were dominant in water (Fig. S3). During summer, dissolved concentrations of OCPs were greater than others at several locations, mainly those in the downstream of HJ within Hubei Province. In sediment (Fig. S4), PCBs were the major pollutants during winter, with greater concentrations at upstream locations. In the DJKR (Fig. 2), OCPs were the predominant pollutants followed by PCBs, except that in sediments of winter, PCBs were predominant residues.

In order to better represent spatial patterns of OCs, the investigated region was divided into 4 sectors: the upper and lower reaches of HJ (separated by the DKJR), the Han Reservoir and the Dan Reservoir. In winter, dissolved OCPs were significantly different between the upper reach and the lower reach of HJ (One-Way ANOVA, $p = 0.032$), as well as between HR and DR (One-Way ANOVA, $p = 0.006$) (Fig. 3). Whereas in summer, dissolved OCPs were not significantly different among the 4 sectors. In sediments, spatial variation was generally not significant during summer or winter, except between HJ up-stream and DR in summer (One Way ANOVA, $p = 0.014$). Spatial distributions of PCBs (Fig. S5) among sectors did not vary significantly for most of the cases, except for between the upper reach of HJ and DR in sediment of summer (One Way ANOVA, $p = 0.009$). Spatial distributions of PBDEs (Fig. S6) were significantly different between the upper reach of HJ and DR in water during both winter (One Way ANOVA, $p = 0.0001$) and summer (One Way ANOVA, $p = 0.032$).

3.3. Phase partition of OCs between water and sediment

OCs investigated in the present study are generally hydrophobic, and thus tend to be absorbed by sediment and suspended particulates in water. Partitioning of OCs between water and sediment is important for understanding their fate in aquatic systems, as well as for accurate assessment of their ecological risk, given that the dissolved phase of contaminants were more bioavailable for most aquatic species (Eggleton and Thomas, 2004). Results of previous studies have shown that the partition coefficient (Kp) between sediment and water was controlled not only by the octanol-water partition coefficient (Kow) of compounds, but also by the total organic carbon (TOC) fraction in sediment (Chiou et al., 1983; Gouin, 2003) and the dissolved organic carbon (DOC) in water (Delgado-Moreno et al., 2010; Gauthier et al., 1987). Therefore, the Kp values of the OCs were plotted against both TOC and DOC (Fig. 4). The Kp of OCPs between sediment and water were significantly and negatively correlated with DOC content in both wet and dry seasons ($p < 0.05$), but the correlation between Kp and sediment TOC was not significant during either season. This result was consistent with the observation that DOC is inversely proportional to Kp values of hydrophobic compounds by increasing their total concentration in water, due to their high affinity to organic matters (Chiou et al., 1986; Wang et al., 2011b). The poor correlation between Kp and TOC of sediments might suggest that partitioning between water and sediment was not at steady state and the possible reasons included transport, mixing of pollutants, depositional mechanisms of sediments, input of

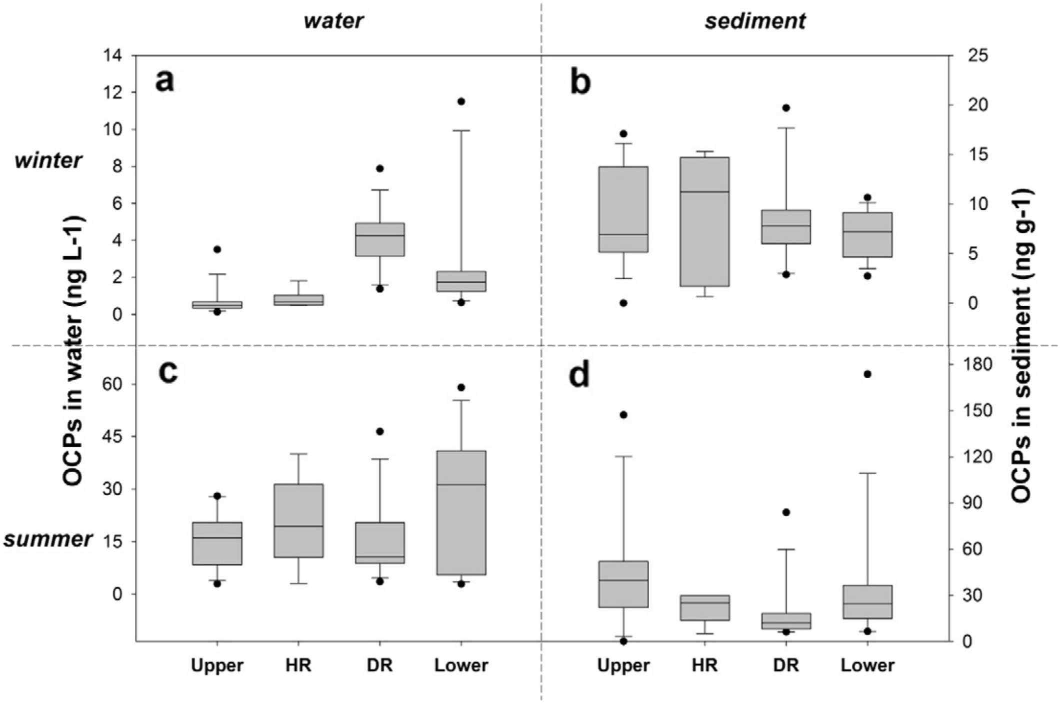

Fig. 3. Distribution of OCPs in (a) water of winter, (b) sediment of winter, (c) water of summer and (d) sediment of summer.

pollutants, as well as their combined effects (Mai et al., 2005). The Kp of PCBs was not significantly, linearly correlated with either DOC or TOC, during winter or summer. Kp values for PBDEs were significantly ($p < 0.05$) and negatively correlated with both DOC and TOC during winter. This result suggested that the PBDEs partition between two phases was more near a steady state during winter, whereas in summer, neither TOC nor DOC was significantly correlated with Kp. This result indicates that partitioning of PBDEs was not at steady state, which might be due to inputs of PBDEs caused by rainfall during summer (Chen et al., 2009).

3.4. Assessments of hazard and risk

3.4.1. Level I ERA

SSDs were developed based on estimates for chronic no effect concentrations derived from acute toxic values such as LC50 and EC50 (Table S3), by use of an ACR. Since it has been speculated that SSD derived from native species might provide more appropriate protection for the local organisms (Jin et al., 2015b), for endosulfan, heptachlor, HCHs and DDT, only toxicity data for species endemic to China were used to construct their respective SSDs. However, toxicity data of resident species in China was sparse for other OCs such as DDD, DDE, endosulfan sulfate and heptachlor epoxide, thus nonnative species were also included in construction of SSDs for those compounds (Fig. 5). HC5 with 50% confidence intervals and PNEC with AF of 1 or 5 were listed in Table 3. HQs calculated as the ratio of OCs concentrations and PNECs at AF of 5 were shown (Fig. 6). The HQs of endosulfan sulfate during winter and heptachlor epoxide during summer exceeded a threshold of 1.0, which indicated significant risk to aquatic organisms. HQs of both endosulfan and endosulfan sulfate in summer were between 0.3 and 1.0, which suggests less ecological risks for these chemicals. HQs for other chemicals were all <0.3, which indicated negligible risks to aquatic organisms (Jin et al., 2015a). For PNEC based on an AF of 1, mean HQs for each toxicants were all <0.3 (data not shown).

3.4.2. Level II ERA

When comparing the distribution of concentrations of OCs in the environment with point effect values of PNEC, the probabilities for the

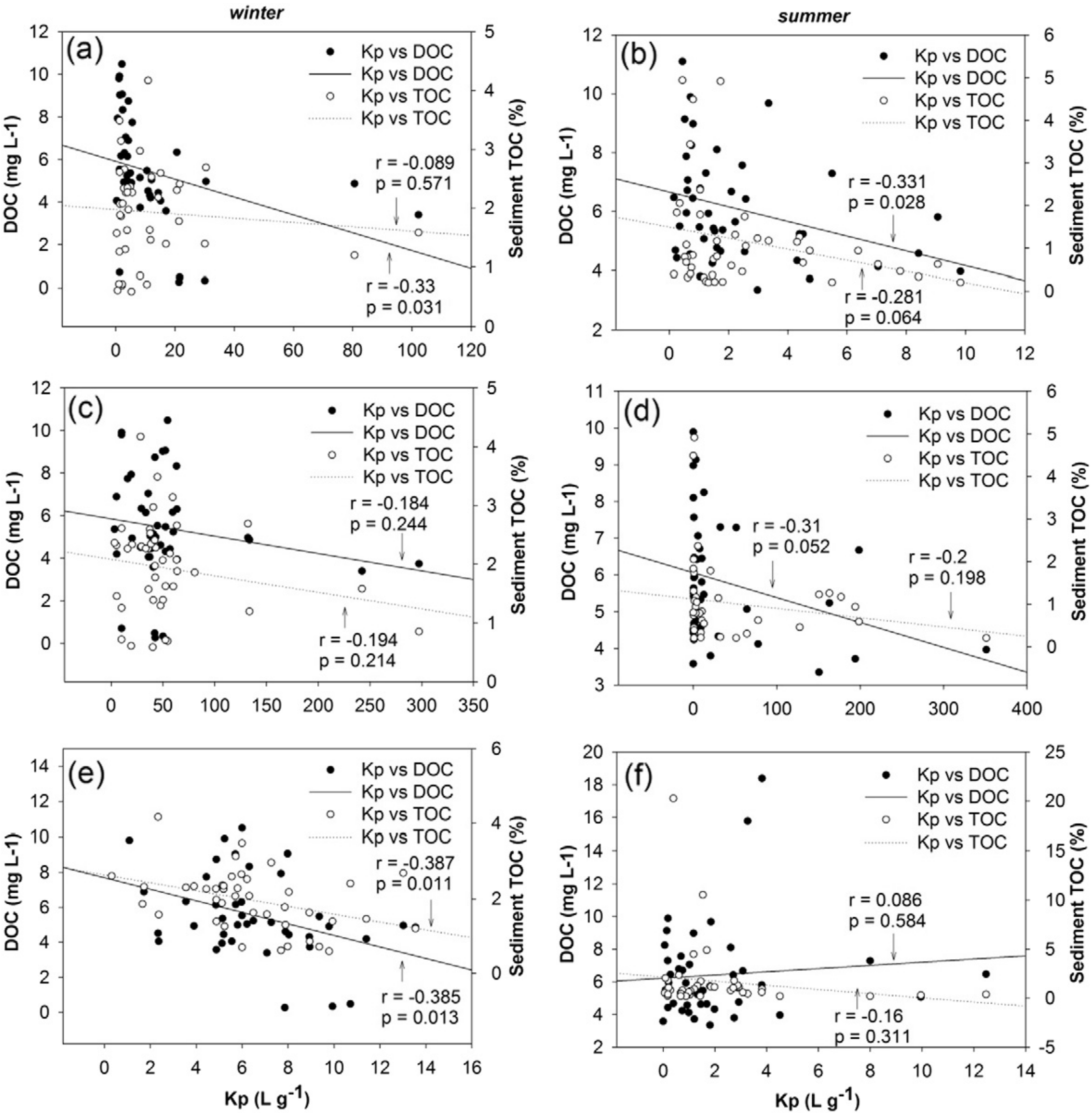

Fig. 4. Linear correlation analysis of the water-sediment partition coefficient (Kp) plotted against the dissolved organic carbon concentration in water (DOC, mg L^{-1}, solid circle and solid line) and total organic carbon fraction in sediment (TOC, %, open circle and dotted line). (a) OCPs in winter, (b) OCPs in summer, (c) PCBs in winter, (d) PCBs in summer, (e) PBDEs in winter, and (f) PBDEs in summer.

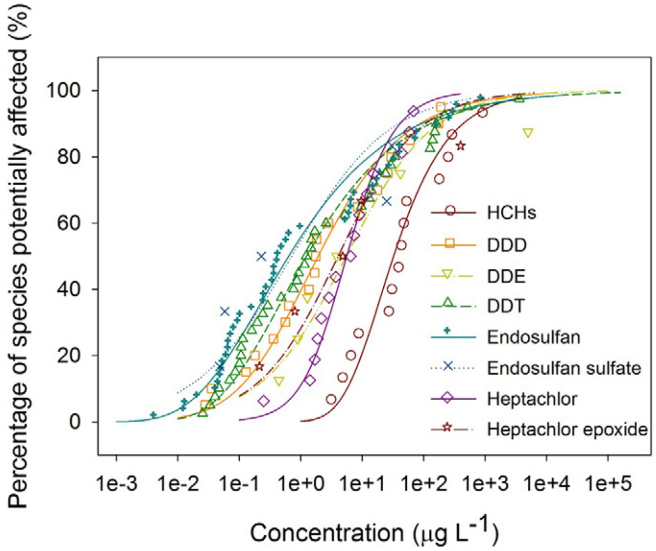

Fig. 5. Species sensitivity distribution curves (SSDs) of various OCs.

field exposure of OCs exceeding the PNEC were acquired (Table 3). Applying an AF of 1, the probabilities for all chemicals exceeding the PNEC were <10%, which suggested negligible risk to the local species (Wang et al., 2009). Whereas when an AF of 5 was applied, probabilities of exceeding the PNEC for endosulfan sulfate in winter was 35%, and probabilities of exceedance for heptachlor epoxide during summer was 51%, which indicated that 35% and 51% of samples from HJ and DJKR would cause adverse effect to >5% of the freshwater species, because of endosulfan sulfate and heptachlor epoxide, respectively. Furthermore, the proportion of aquatic species potential affected by exposure to OCs were also evaluated (Table 3). When using geometric mean concentrations, none of the individual OCs would affect >5% of the aquatic species. However, in the worst case by using maximum OCs concentrations, endosulfan sulfate would affect 9% and 5% of species during winter and summer, respectively, and heptachlor epoxide would affect 5% species in summer.

3.4.3. Level III ERA

JPCs were developed based on probability distributions for exposures (determined environmental concentrations of OCs) and effects (toxicity data for corresponding OCs) (Fig. 7). Overall risks were assessed quantitatively by use of the area under the JPC, an index that gives an integrated measure of probability of environmental concentrations exceeding various thresholds of effects. A JPC area larger than 0.1% indicates potential risk, and an JPC area >1% were considered to be unacceptable (Li and You, 2015). JPC areas for endosulfan, endosulfan sulfate and heptachlor epoxide were 1.6%, 4.5% and 5.6%, respectively. These results suggested risks posed by these contaminants to the local aquatic ecosystem in the Han River and Danjiangkou Reservoir. JPC areas for the other OCs were <0.1%. When the hazard effect level was set at 5% or 10% of species affected, the corresponding probability of the exposure concentrations to exceed that value were 33.4% and 8.5% for endosulfan sulfate, 9% and 3.5% for endosulfan, 24.4% and 15.9% for heptachlor epoxide, respectively. For other OCs such as DDT, 5% of species would be affected <0.01% of time.

3.4.4. Uncertainty and limitations

Uncertainties in the probabilistic assessment presented here can be attributed to limitations in availability of data, use of non-native species for construction of SSDs and JPCs, the use of acute toxicity data due to non-available chronic values, as well as use of the ACR to convert acute data to chronic values (Wang et al., 2009). For instance, various ecosystems might contain different taxa that might exhibit different sensitivities to contaminants. Thus, a concentration of contaminant might be safe in one ecosystem but not in others. Use of non-native species' toxicity data for ecological risk assessment can be controversial (Maltby et al., 2005). Nevertheless, at present, due to the paucity of enough toxicity data for native species, especially in China, this limitation cannot be avoided.

There are some underlying assumptions of probabilistic assessments of risk. The extent to which these assumptions are violated determines accuracies of assessments. For instance, it is assumed that data collected for estimates of exposure and responses are robust. Also, resolution of thresholds for effects is a function of the number of taxa considered. For instance, if 10 species are included resolution of the assessment would be no better than 10%. Also, selection of species used to generate the SSD has a significant effect on accuracies of assessments. Since it is assumed that the entire range of possible sensitivities is covered, if this is not true a systematic bias would be introduced. Finally, use of probabilistic methods can lead to misunderstandings with risk managers. Specifically, the use of the HC5 as a measure of *de minimus* risk is often questioned. For instance, use of the LC50 would mean that 50% of individuals of 5% of species would be expected to die. If those

Table 3
Results of the hazardous concentration affecting 5% species (HC5) with 50% confidence intervals and predicted no effect concentration (PNEC) at various application factors (AF) derived from species sensitivity distributions (SSDs). Results of level II risk assessment: potential affected fraction (PAF) at geometric mean (Geomean) and maximum (Max) environmental concentrations, as well as the probability (prob.) of measured concentrations exceeding PNECs.

	HC5 (ng L^{-1})	AF	PNEC (ng L^{-1})	Winter			Summer		
				PAF		Prob.	PAF		Prob.
				Geomean	Max		Geomean	Max	
HCHs	3800	1	3800	0%	0%	0%	0%	0%	0%
	(3000–6100)	5	760			0%			0%
DDD	42	1	42	0%	0%	0%	0%	0%	0%
	(30–72)	5	8.4			0%			0%
DDE	50	1	50	0%	0%	0%	0%	1%	0%
	(37–192)	5	10			0%			0%
DDT	33	1	33	0%	0%	0%	0%	0%	0%
	(28–44)	5	6.6			0%			0%
Endosulfan	13	1	13	0%	0%	0.02%	0%	0%	0%
	(11–18)	5	2.6			0.10%			0.19%
Endosulfan sulfate	3	1	3	1%	9%	2.30%	1%	5%	0%
	(3–24)	5	0.6			35%			0.04%
Heptachlor	520	1	520	0%	0%	0%	0%	0%	0%
	(300–560)	5	104			0%			0%
Heptachlor epoxide	50	1	50	0%	1%	0%	1%	5%	1.70%
	(41–219)	5	10			0%			51%

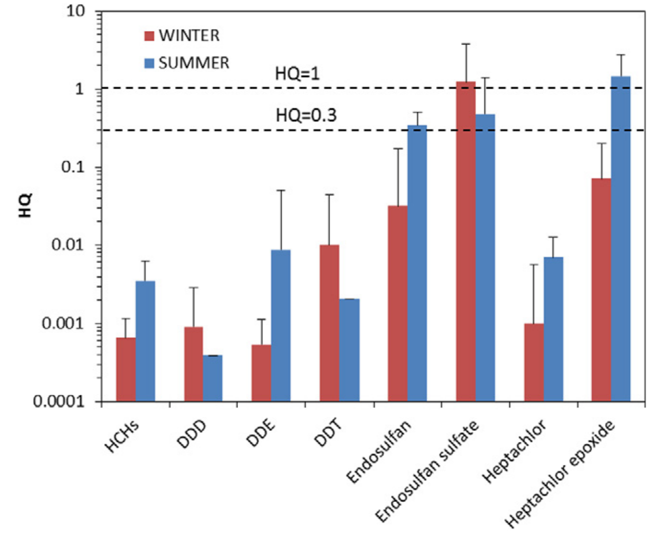

Fig. 6. Hazard quotients (HQs) of OCs detected in Hanjiang River and Danjiangkou Reservoir based on predicted no effect concentrations (PNECs) derived by use of the SSD method, with an application factor (AF) of 5.

species were cornerstone species of ecosystems, that could result in a loss of ecosystem services. The SSD is most useful in identifying the taxa that are most sensitive to chemical stressors. This information along with understanding of the structure and functions of ecosystems can then be used to make judgments of the likelihood that critical ecosystem services might be adversely affected.

LC50 values are based on studies conducted under laboratory conditions of constant exposure with 100% of the chemical tested being available. Under field conditions organisms are generally not exposed continuously for long periods so that there is potential for recovery through repair of damage caused by chemical stressors. Also, under field conditions, due to dissipation and interactions with various accessory factors such as dissolved organic carbon or particulates, the available fractions of most organic chemicals are generally much <100%. That means predicted hazards or risks are generally greater than what would be observed under field conditions in more natural media. So the results of assessments reported here need to be considered as guidelines to assist in decision making, rather than absolute “regulatory bright lines”.

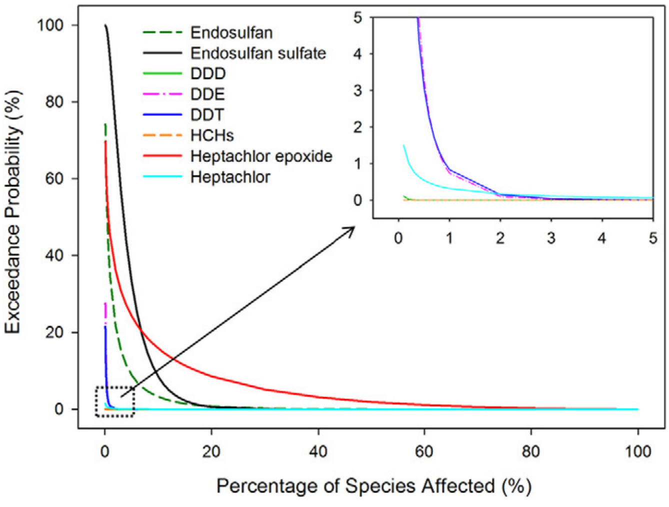

Fig. 7. Joint probability curves (JPC) derived by use of the Probabilistic Risk Assessment Tool (PRAT) for level III ecological risk assessment of the OCs in Hanjiang River and Danjiangkou Reservoir.

3.4.5. Risks to health of humans

Because the Danjiangkou Reservoir is source of water for the South-to-North Water Diversion Project, which is intended to provide drinking water for the population in Northern China, risks to health of humans posed by drinking water or dermal contact such as showering were also assessed. Chemical-specific parameters, such as *RfD* and *SF* are listed in Table S4. Lifetime risk of additional cancers caused by OCs in water from HJ and DJKR were generally $<10^{-6}$, except for OCPs during summer (Table S5). These results suggested that carcinogenic risk was *de minimus* during winter, but slightly greater in summer. Risk of additional cancers to humans was contributed mostly by heptachlors. For non-cancer risk, HIs were all much <1.0, which indicates that non-cancer hazards were *de minimus*. Concentrations of OCs were also compared to corresponding maximum contaminant levels (MCLs), set by the US National Primary Drinking Water Regulations (40 CFR Part 141). For α-HCH, β-HCH, γ-HCH, Endosulfans, *p*, *p*′-DDD, *p*, *p*′-DDE, *p*, *p*′-DDT, heptachlor, heptachlor-epoxide and PCBs, MCLs are 2.6, 9.1, 9.8×10^{2}, 6.2×10^{4}, 0.31, 0.22, 0.22, 7.9×10^{-2}, 3.9×10^{-2} and 6.4×10^{-2} ng L^{-1}, respectively. For most OCs, measured concentrations were less than their MCLs. However concentrations of heptachlor, heptachlor-epoxide and PCBs exceeded their respective MCLs during both seasons. This result suggests that OCs in water from HJ and DJKR might pose potential hazards to health of humans through consumption of water. Nevertheless, in this analysis, only exposure via consumption of raw drinking water is considered. Uncertainties can result because some proportion of OCs would likely be removed during treatment of water (Hu et al., 2013; Shi et al., 2016). Furthermore, potential exposure via the diet from consumption of fishes exposed to the OCs could be greater (Wang et al., 2013; Wang et al., 2011a), but was not considered in this study, which would also contribute to the uncertainties of the risk assessment.

4. Conclusions

Organohalogen contaminants (OCs) were prevalent in the Han River and Danjiangkou Reservoir, though their concentrations were relatively small. Ecological risk assessed using a tiered probabilistic approach indicated risks to aquatic organisms caused by some OCs such as heptachlor epoxide, and potential risk to human health through water consumption. Nevertheless, the assessment of risks did not take into consideration combined adverse effects of the chemicals, thus might underestimate their risk. Also, alternative indirect pathways of exposure such as bioaccumulation into dietary items were not considered. Therefore, further work still need be performed for more accurate risk assessment and management of toxic chemicals in this region.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2017.01.194.

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Supplementary Material:

Tiered probabilistic assessment of organohalogen compounds in the Han River and Danjiangkou Reservoir, central China

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Table S1. Comparisons of OCs in water (ng L^{-1}) observed in this study with those from other regions.

Table S2. Comparisons of concentrations of OCs (ng.g^{-1}dw) observed in sediments during this study with those in other regions.

Table S3. Toxic potencies (LC50) used to develop SSDs, where the SMAVs (species mean acute values) refer to the geometric mean value of the toxicity data if one species have more than one acute values for a single compound. Data acquired from (Yan, 2015).

Table S4. Slope factors (*SF*) and reference doses (*RfD*) for OCs (data from USEPA IRIS).

Table S5. Carcinogenic risks and hazard indices for non-cancer effects on health of humans posed by OCs in water from the Hang River and Danjiangkou Reservoir, through water consumption and dermal contact.

Figure S1. Profiles of relative **c**ompositions OCPs in the surface water samples collected from the Han River and Danjiangkou Reservoir during (a) winter and (b) summer, as well as in the sediment samples during (c) winter and (d) summer.

Figure S2. Relative proportions of congeners of: (a) PCBs and (b) PBDEs from Han River and Danjiangkou Reservoir.

Figure S3. Spatial distributions of concentrations of OCs in the Han River. Upward columns represent OCs concentrations in winter, while downward columns represent OCs concentrations in summer.

Figure S4. Spatial distribution of concentrations of OCs in the Han River. Upward columns represent concentrations of OCs during winter, while downward columns represent concentrations of OCs during summer.

Figure S5. Spatial distribution of concentrations of ΣPCBs in: (a) water during winter, (b) sediment during winter, (c) water during summer and (d) sediment during summer.

Figure S6. Spatial distribution of concentrations of ΣPBDEs in: (a) water during winter, (b) sediment during winter, (c) water during summer and (d) sediment during summer.

Chemicals and materials. Chemicals considered in this study included 12 OCPs (α-HCH, β-HCH, γ-HCH, δ-HCH, *p,p'*-DDE, *p,p'*-DDD, *p,p'*-DDT, heptachlor, heptachlor epoxide, α-endosulfan, β-endosulfan, and endosulfan sulfate), 7 indicator PCB congeners defined by GEMS (Global Environmental Monitoring System)/Food (WHO Regional Office for Europe, 2004), which included PCB-28, 52, 101, 118, 138, 153 and 180, following the nomenclature described by Ballschmiter and Zell (1980), as well as the 7 PBDEs of primary interest identified by the USEPA Method 1614, which includes 2,4,4'-TrBDE, 2,2',4,4'-TeBDE, 2,2',4,4',5-PeBDE, 2,2',4,4',6-PeBDE, 2,2',4,4',5,5'-HxBDE, 2,2',4,4',5',6-HxBDE and 2,2',3,4,4',5',6-HpBDE, numbered respectively as BDE-28, 47, 99, 100, 153, 154 and 183. Standards for the above-listed analytes as well as internal standard pentachloronitrobenzene (PCNB) were purchased from AccuStandard (New Haven, CT, USA). PCB-209, obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany), was used as surrogate standard to determine recoveries during extraction of samples. To minimize possible background contamination of samples, solvents used for extraction were HPLC-grade. C18 solid phase extraction (SPE) cartridges (Sep-Pak, 3cc/500 mg) were purchased from Waters Corporation (Milford, Massachusetts, USA). Florisil (60-100 mesh) and Silica gel (100-200 mesh) were activated at 150 ºC for 10 h and at 180 ºC for 4 h, respectively. 30% (v/m) H_2SO_4 was added to prepare acid silica gel. Copper powder was immersed into 2 N HCl, washed with water and acetone successively before use. Anhydrous sodium sulfate as well as glassware used for extraction were baked at 450 ºC for 4 h just before use to remove organic interferences.

Extraction, identification and quantification. One liter of filtered water samples was loaded through a BondEluent C18 cartridge (500 mg, 3 mL, Supelco) for solid phase extraction (SPE) at a constant flow of 5 mL min^{-1}, which were preconditioned, successively with 10 mL of dichloromethane, followed by methanol then water. After washing the cartridge with 50% methanol in water, the analytes were eluted using 20 mL of dichloromethane. The eluent was evaporated to dryness under a gentle flow of nitrogen, then reconstituted with 100 μL of Hexane for instrumental injection.

Samples of sediment were extracted by use of matrix solid-phase dispersion (MSPD) procedures. One gram of sample was ground thoroughly with 3 g C18 (Silicycle, Inc., Québec, Canada), and transferred to the top of a pre-packed cartridge, which consisted sequentially from bottom to top, of 1 g Na_2SO_4, 1 g florisil, 1 g acidic silica gel, and 2 g activated copper powder. Target analytes were then eluted with 15 mL of dichloromethane. The eluent was concentrated following the same procedure with water sample before injection.

OCPs, PCBs and PBDEs were analyzed using Agilent 7890A gas chromatograph (GC) equipped with an electron capture detector (μECD) and a Model 5975 mass spectrometer (MS) with electron-ionization ion source (EI). The capillary column used was HP-5MS (30 m×0.25 mm i.d. ×0.25 μm) and the carrier gas flow was 1.2 mL min^{-1}. One microliter of sample was injected in splitless mode. The inlet and μECD temperatures were set at 280 °C and 300 °C, respectively. EI temperature was 300 °C, and the energy was 70 eV. MS was operated in scan mode for analytes identification, whereas μECD signals were acquired for quantification. The GC oven was set at 80 °C for 1 min initially, and rose to 190 °C at 15 °C min^{-1}, held for 2 min, further to 220 °C at 8 °C min^{-1}, held for 5 min, and finally to 300 °C at 10 °C min^{-1}, held for 7 min. All the 26 OCs can be analyzed in a single run of 34 min.

Assessment of risks to health of humans. Exposures (E) to OCs through consumption of drinking water and dermal absorption were calculated (Equations S1 and S2, respectively).

$$E_{drinking} = C_B \times \frac{IR_w \times EF \times ED}{BW \times AT} \tag{S1}$$

$$E_{dermal} = 2 \times 10^{-3} \times k \times C_B \times \sqrt{6 \times t \times TE / \pi} \times \frac{A_{sd} \times EF \times FE \times ED}{BW \times AT \times f} \tag{S2}$$

where C_w represents concentrations of OCs (mg L^{-1}), IR_w is the daily amount (2 L day^{-1}) of water consumed, EF is frequency of exposure (365 days year^{-1}), ED is duration (30 years) of exposure, BW is the average body weight of adults (60 kg), AT is the mean exposure time (365 days×70 years=25550 days), k is the dermal adsorption factor (0.001 cm h^{-1}), t is the lag time per event (1h); TE is duration of event (0.4 h), A_{sd} represents the skin surface area available for contact (16,600 cm^2), FE is frequency of exposure via the dermal route (0.3 times day^{-1}), f is the fraction absorbed (unitless, 1).

Risk of cancers was calculated (Equations S3 and S4), based on the oral slope factor (SF, per mg kg^{-1} day^{-1}). Risks less than 10^{-6} were considered *de minimus*, and risks between 10^{-4} and 10^{-6} was considered small. Risks between 10^{-3} and 10^{-4} were considered moderate, whereas risks greater than10^{-3} were considered unacceptable.

$Risk=SF\times E$ $\quad$ $Risk < 0.01$.. (S3)

$Risk=1-e^{(-SF\times E)}$ $\quad$ $Risk \geq 0.01$.. (S4)

The non-cancer hazard index (HI) was calculated (Equation S5)

$HI=E/RfD$…..………………..……………………………………………….(S5)

where RfD is the chronic reference dose (mg kg^{-1} day^{-1}). HI larger than one indicates non-cancinogenic risk, whereas HI less than 1.0 indicates small risk (Chien et al., 2002).

Chemical-specific parameters such as RfD and SF are listed in **Table S4**.

Table S1. Comparisons of OCs in water (ng L^{-1}) observed in this study with those from other regions.

study area	sampling period	compound number	Range	Mean	reference
OCPs					
Han River and Danjiangkou Reservoir, China	2014-2015	12	0.14-11.50 [a] 2.87-58.99 [b]	2.23 [a] 19.34 [b]	this study
Pearl River Delta, China	2008-2009	20	6.64-57.06 [a] 17.02-26.58 [b]	25.07 [a] 22.32 [b]	(Sun et al., 2014)
Qiantang River, China	2005	13	7.68-269.4		(Zhou et al., 2006)
Lake Chao, China	2009	24	1.6–1,678.6	132.4	(Liu et al., 2013)
Mumbai coastline, India		7	3.17-49.13	17.87	(Pandit et al., 2006)
PCBs					
Han River and Danjiangkou Reservoir, China	2014-2015	7	0.55-9.03 [a] 0.04-12.17 [b]	0.97 [a] 2.13 [b]	this study
Baiyangdian Lake, China	2008	41	19.46-131.62	45.35	(Dai et al., 2011)
Tonghui River, China	2002	12	31.58-344.9	105.5	(Zhang et al., 2004)
Venice Lagoon	2001	6	0.25-0.792		(Matteo et al., 2005)

Houston Ship Channel, Texas	2002-2003	209	0.49-12.49		(Howell et al., 2008)
Seine Estuary, France	2002-2005	8	2.0-21.2	7.0	(Cailleaud et al., 2007)
PBDEs					
Han River and Danjiangkou Reservoir, China	2014-2015	7	1.34-2.29 [a] 0.35-4.99 [b]	1.58 [a] 0.78 [b]	this study
Tai Lake, China	2004	10		1.2 ± 1.7	(Qiu et al., 2010)
Seawater in Hong Kong, China	2005	8	0.0311-0.1187	0.0707	(Wurl et al., 2006)
Pearl River Estuary, China	2005	7	26.1-156.9		(Luo et al., 2008)
Lake Shihwa, Korea	2008	23	0.16-11.0		(Moon et al., 2012)

[a]: winter; [b]: summer

Table S2. Comparisons of concentrations of OCs (ng.g^{-1}dw) observed in sediments during this study with those in other regions.

study area	sampling period	compound number	range	Mean	reference
OCPs					
Han River and Danjiangkou Reservoir, China	2014-2015	12	0.67-19.70 [a] 4.99-173.57 [b]	8.22 [a] 32.23 [b]	this study
Pearl River Delta, China	2008-2009	20	10.05-447.13 [a] 9.33-598.65 [b]	202.77 [a] 161.24 [b]	(Sun et al., 2014)
Qiantang River, China	2005	13	23.11-316.5		(Zhou et al., 2006)
Lake Chao, China	2009	24	0.9–36.9	13.7	(Liu et al., 2013)
Mumbai coastline, India		7	4.3-25.8	15.58	(Pandit et al., 2006)
PCBs					
Han River and Danjiangkou Reservoir, China	2014-2015	7	4.27-227.54 [a] nd-26.44 [b]	39.67 [a] 4.98 [b]	this study
Baiyangdian Lake, China	2008	41	5.96-29.61	18.91	(Dai et al., 2011)
Hai River, China	2007	32	0.177-253	99.1	(Zhao et al., 2010)
Hugli Estuary, India	2005	13	0.18-2.33		(Guzzella et al., 2005)

Mekong River Delta, Vietnam	2003-2004	Aroclor 1254	0.039-9.2	0.89	(Minh et al., 2007)
PBDEs					
Han River and Danjiangkou Reservoir, China	2014-2015	7	0.67-20.58 [a] nd-6.83 [b]	9.55 [a] 1.16 [b]	this study
Hong Kong marine waters	2004	15	1.7-52.1	9.77	(Liu et al., 2005)
Pearl River Delta, China	2002-2004	9	0.04-94.7		(Mai et al., 2005)
Coastal East China Sea	2006-2007		nd-8	1.6	(Li et al., 2012)
Masan Bay, South Korea	2008	29	1.3-19	5.7	(Hong et al., 2010)
Scheldt River, Netherland	2001	5	0.6-17.6	2.4	(de Boer et al., 2003)
Hadley Lake, USA			5.2-37.6	13.9	(Dodder et al., 2002)

[a]: winter; [b]: summer

Table S3. Toxic potencies (LC50) used to develop SSDs, where the SMAVs (species mean acute values) refer to the geometric mean value of the toxicity data if one species have more than one acute values for a single compound. Data acquired from (Yan, 2015).

Species	**Distribution**	**SMAVs(μg L^{-1})**
Endosulfan		
Bu fo bufo	China	430
Bu fo melanostictus	China	129
Rana limnocharis	China	12
Cypiris subglobosa	China	1
Daphnia carinata	China	478
Daphnia longispina	China	0.3
Monia macrocopa	China	366
Macrobrachium nipponense	China	1.25
Procambarus clarkii	China	24
Ceriodaphnia dubia	China	162
Daphnia magna	China	183
Gammarus lacustris	China	6.09
Leuciscus idus	China	9
Anabas testudineus	China	1.63
Anguilla japonica	China	14
Channa orientalis	China	6.7
Channa punctata	China	2.5
Channa striata	China	4000
Clarias batrachus	China	15.7
Gymnocorymbus ternetzi	China	1.6
Heteropneustes fossilis	China	1.1
Misgurnus anguillicaudatus	China	1.2
Puntius sophore	China	1.3
Tilapia zillii	China	1.76
Oryzias latipes	China	1.5
Poecilia reticulata	China	8.95
Cyprinus carpio	China	0.1
Gasterosteus aculeatus	China	6
Carassius auratus	China	0.316
Ctenopharyngodon idella	China	1.98
Perccottus glehni	China	10.3
Gambusia affinis	China	3.88
Monopterus albus	China	0.499
Tilapia aurea	China	2.31
Aedes aegypti	China	8.396
Culex fatigans	China	150
Eretes sticticus	China	10
Cloeon dipterum	China	160

Hydra viridissima	China	670
Hydra vulgaris	China	810
Brachionus calyciflorus	China	1810
Aplexa hypnorum	China	1890
Cipangopaludina malleata	China	8500
Indoplanorbis exustus	China	21000
Lymnaea stagnalis	China	1000
Physella acuta	China	6400
Planorbis corneus	China	1000
Semisulcospira libertina	China	7400
Heptachlor		
Esox lucius	China	6.2
Gambusia affinis	China	35
Daphnia pulex	China	42
Simocephalus serrulatus	China	47
Cloeon dipterum	China	72
Daphnia magna	China	92.6
Gammarus lacustris	China	53.9
Heteropneustes fossilis	China	162
Poecilia reticulata	China	184
Channa punctata	China	224
Carassius auratus	China	298
Cyprinus carpio	China	380
Tubifex tubifex	China	1100
Aplexa hypnorum	China	1450
Clarias batrachus	China	1702
HCHs		
Gammarus lacustris	China	78
Oryzias latipes	China	120
Hypophthalmichthys nobilis	China	164
Ctenopharyngodon idella	China	218
Daphnia pulex	China	680
Rana limnocharis	China	766
Heteropneustes fossilis	China	978
Cyprinus carpio	China	1091
Carassius auratus	China	1192
Daphnia magna	China	1320
Channa punctata	China	4490
Poecilia reticulata	China	6250
Microhyla ornata	China	7270
Clarias batrachus	China	22804
DDT		
Bosmina longirostris	China	0.63
Ceriodaphnia dubia	China	0.83

Chironomus tentans	China	1
Daphnia pulex	China	1.17
Daphnia magna	China	1.73
Esox lucius	China	2.14
Simocephalus serrulatus	China	2.5
Carassius auratus	China	2.65
Gammarus lacustris	China	2.66
Aedes aegypti	China	2.83
Clarias batrachus	China	3.97
Poecilia reticulata	China	4.9
Rhodeus sericeus	China	6
Culex pipiens	China	7.2
Daphnia carinata	China	12
Oryzias latipes	China	19
Eretes sticticus	China	21.5
Chironomus plumosus	China	23
Cypridopsis vidua	China	28.5
Channa punctata	China	30.6
Carassius carassius	China	36.6
Gambusia affinis	China	37
Brachionus calyciflorus	China	42
Barbus dorsalis	China	64.3
Lumbriculus variegatus	China	130
Misgurnus anguillicaudatus	China	240
Monia macrocopa	China	324
Cyprinus carpio	China	350
Rana limnocharis	China	377
Procambarus clarkii	China	600
Channa striata	China	730
Cloeon dipterum	China	850
Heteropneustes fossilis	China	3162
Physella acuta	China	3500
Semisulcospira libertina	China	3800
Tubifex tubifex	China	4000
Indoplanorbis exustus	China	5500
Cipangopaludina malleata	China	13000
Hirudo nipponia	China	90000
DDD		
Bu fo woodhouse	USA	212
Pseudacris triseriata	USA	447
Xenopus laevis	else	4768
Daphnia magna	China/USA	8.9
Daphnia pulex	China/USA	3.2
Simocephalus serrulatus	China/USA	4.5

Caecidotea brevicauda	USA	16
Palaemonetes kadiakensis	USA	0.7
Gammarus lacustris	China/USA	0.884
Micropterus salmoides	USA	42
Sander vitreus	USA	14
Ictalurus punctatus	USA	1500
Lepomis macrochirus	USA	43.5
Pimephales promelas	USA	4400
Oncorhynchus mykiss	USA	70
Ischnura verticalis	USA	34
Pteronarcys californica	USA	647
Cypridopsis vidua	China/USA	45
Polycelis felina	else	740
DDE		
Xenopus laevis	else	124986
Hyalella azteca	USA	10.99
Lepomis macrochirus	USA	240
Oncorhynchus mykiss	USA	32
Salmo salar	USA	96
Chironomus dilutus	USA	22.3
Polycelis felina	else	1050
Endosulfan sulfate		
Oncorhynchus mykiss	USA	1.45
Jappa kutera	else	1.2
Daphnia magna	China/USA	625
Daphnia carinata	China/USA	756
Hyalella azteca	USA	5.7
Heptachlor epoxide		
Daphnia magna	China/USA	240
Lepomis macrochirus	USA	5.3
Poecilia reticulata	China/USA	120
Oncorhynchus mykiss	USA	20
Tubifex tubifex	China/USA	10000

Table S4. Slope factors (*SF*) and reference doses (*RfD*) for OCs (data from USEPA IRIS).

Compounds	*SF*(mg/kg/day)$^{-1}$	*RfD* (mg/kg/day)
α-HCH	6.3	0.0005
β-HCH	1.8	0.0002
γ-HCH	1.3	0.0003
δ-HCH[a]	0.35	0.0003
Heptachlor	4.5	0.0005
Heptachlor epoxide	9.1	0.000013
∑DDTs	0.35	0.0005
∑Endosulfan[b]		0.006
Tri-/Tetra-CB	2	0.00007[c]
Penta-/Hexa-/Hepta-CB	2	0.00002[d]
PBDEs		0.0001[e]

[a] data of ∑HCHs adopted

[b] data of *α*-Endosulfan and *β*-Endosulfan adopted

[c] data of Aroclor 1016 adopted

[d] data of Aroclor 1254 adopted

[e] data of BDE47 and BDE 99 adopted

Table S5. Carcinogenic risks and hazard indices for non-cancer effects on health of humans posed by OCs in water from the Hang River and Danjiangkou Reservoir, through water consumption and dermal contact.

	winter		summer	
	carcinogenic	HI	carcinogenic	HI
∑ HCHs	1.4E-08±1.1E-08	2.5E-05±2.2E-05	1.2E-07±1.6E-07	1.2E-04±6.7E-05
∑ DDTs	4.0E-10±1.1E-09	2.3E-06±6.4E-06	5.2E-10±2.1E-09	3.0E-06±1.2E-05
∑ heptachlors	1.0E-07±1.7E-07	8.0E-04±1.4E-03	2.0E-06±1.7E-06	1.6E-02±1.5E-02
∑ endosulfans		2.0E-06±3.9E-06		2.8E-06±1.6E-06
∑OCPs	*1.2E-07±1.7E-07*	*8.3E-04±1.4E-03*	*2.1E-06±1.8E-06*	*1.6E-02±1.5E-02*
∑PCBs	*2.8E-08±3.6E-08*	*5.0E-04±3.7E-04*	*6.1E-08±9.0E-08*	*6.3E-04±8.8E-04*
∑PBDEs		*2.3E-04±2.8E-05*		*1.1E-04±1.1E-04*

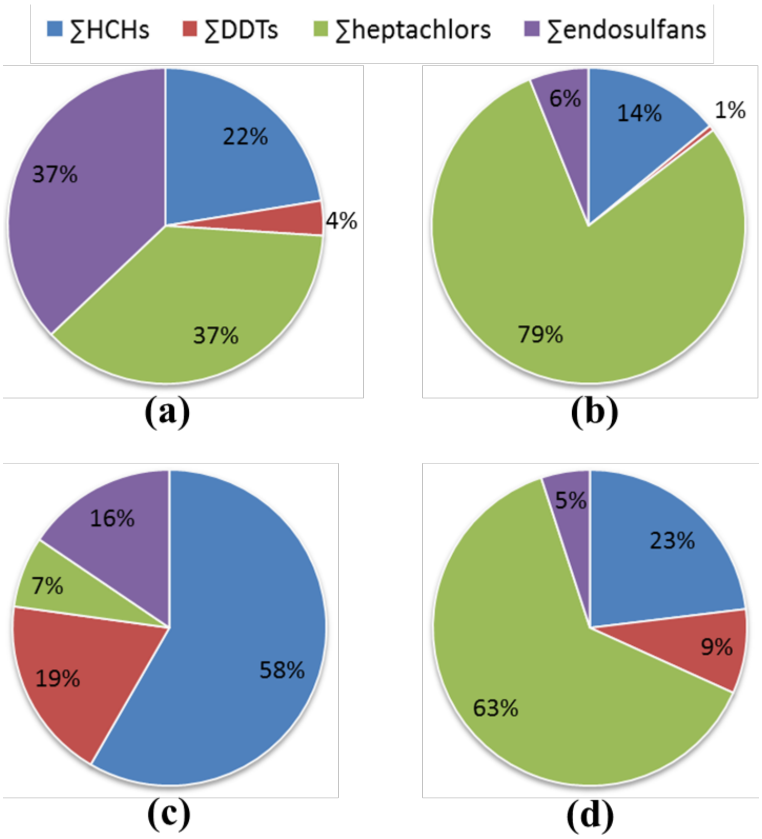

Figure S1. Profiles of relative **c**ompositions OCPs in the surface water samples collected from the Han River and Danjiangkou Reservoir during (a) winter and (b) summer, as well as in the sediment samples during (c) winter and (d) summer.

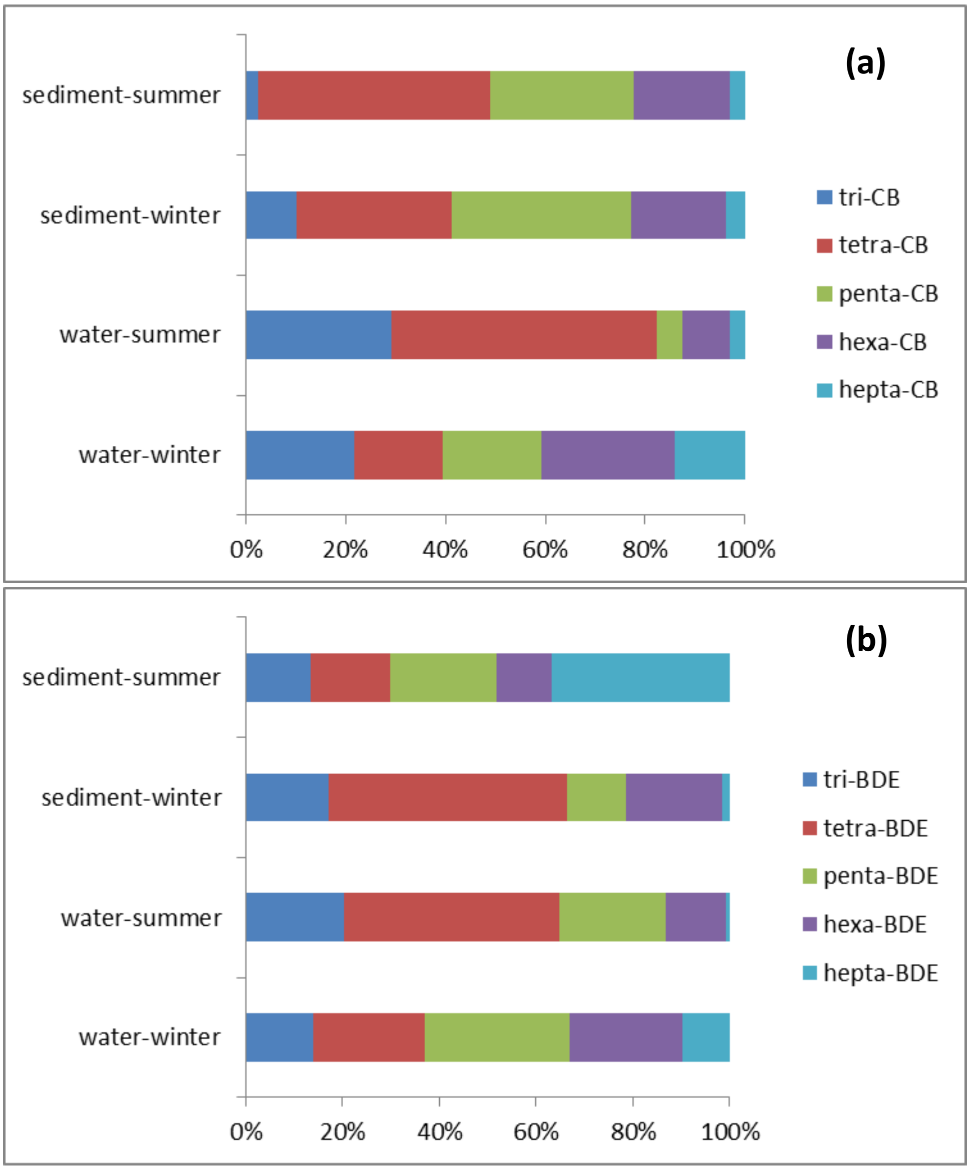

Figure S2. Relative proportions of congeners of: (a) PCBs and (b) PBDEs from Han River and Danjiangkou Reservoir.

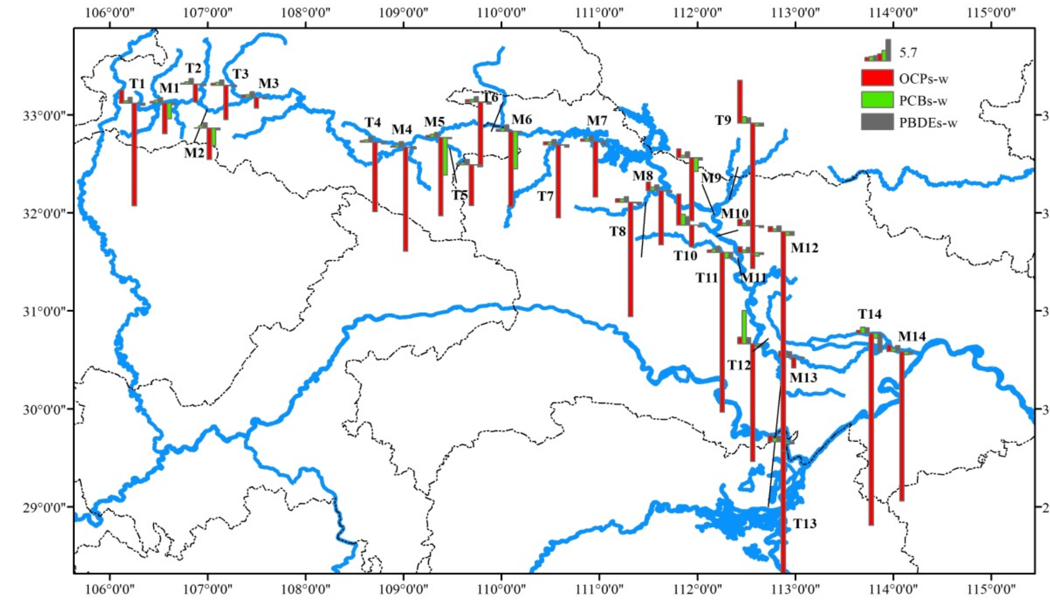

Figure S3. Spatial distributions of concentrations of OCs in the Han River. Upward columns represent OCs concentrations in winter, while downward columns represent OCs concentrations in summer.

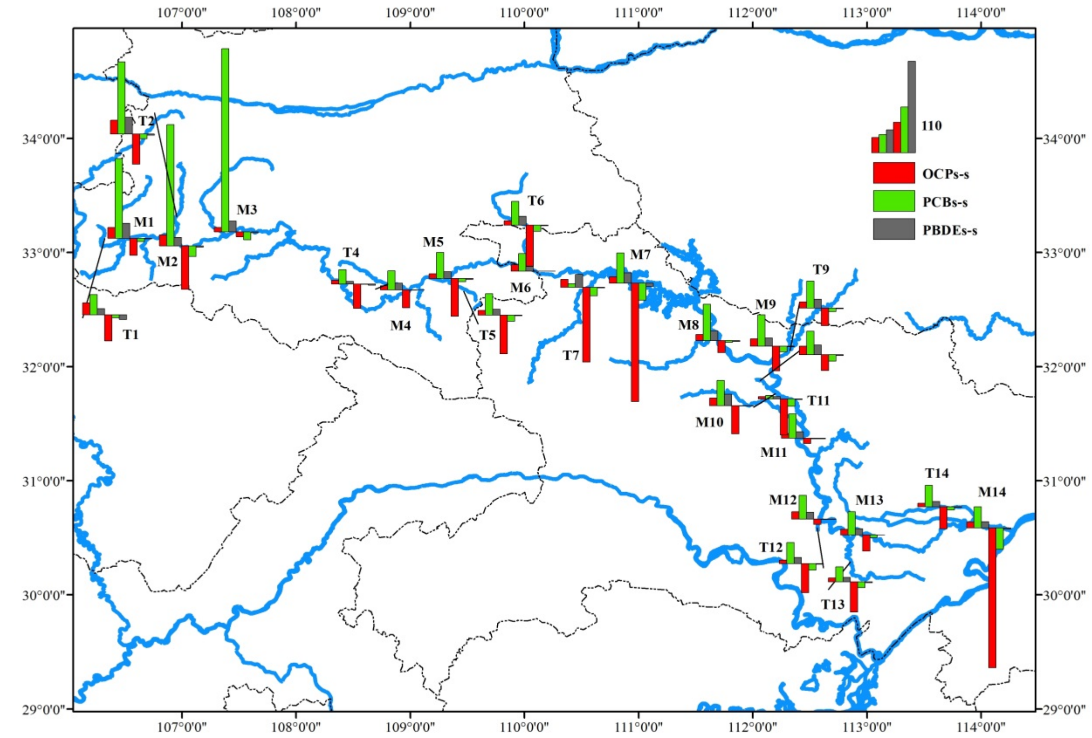

Figure S4. Spatial distribution of concentrations of OCs in the Han River. Upward columns represent concentrations of OCs during winter, while downward columns represent concentrations of OCs during summer.

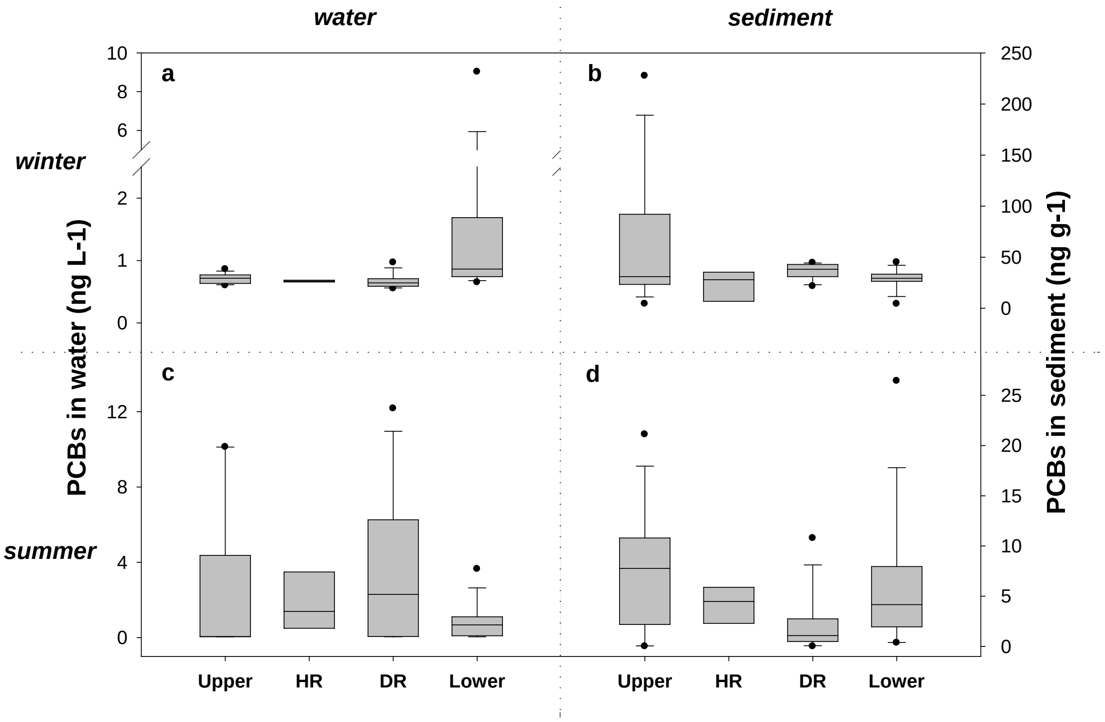

Figure S5. Spatial distribution of concentrations of ΣPCBs in: (a) water during winter, (b) sediment during winter, (c) water during summer and (d) sediment during summer.

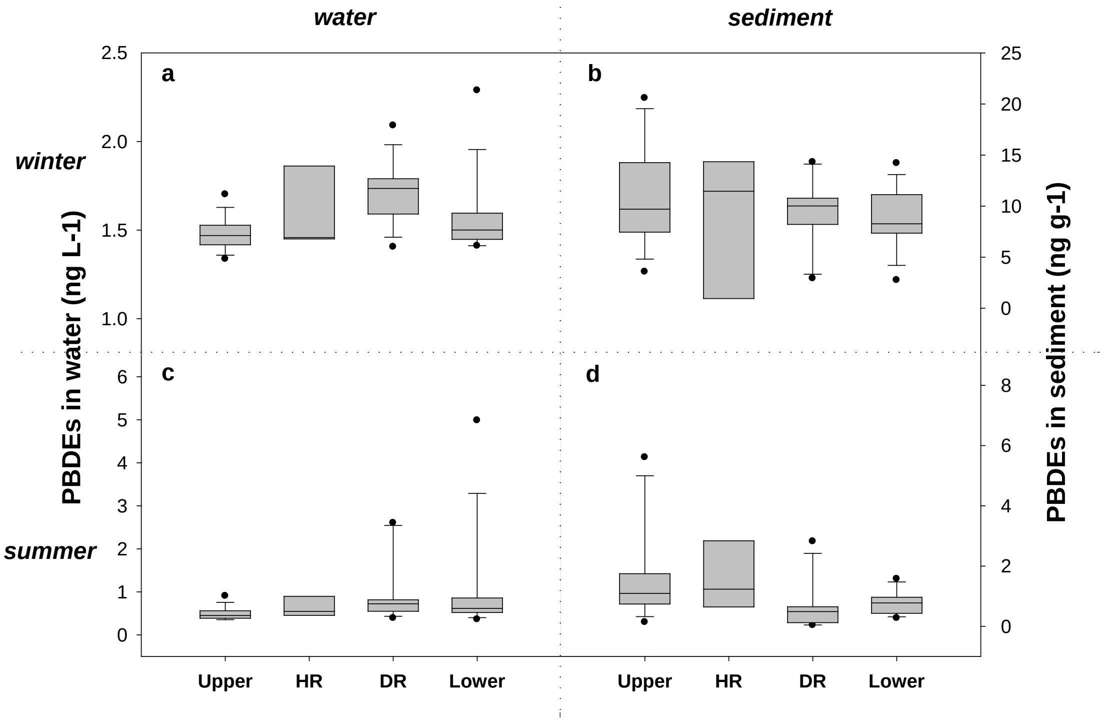

Figure S6. Spatial distribution of concentrations of ΣPBDEs in: (a) water during winter, (b) sediment during winter, (c) water during summer and (d) sediment during summer.

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