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RISK ASSESSMENT ARTICLES

Ecological Risk Assessment of Organochlorine Pesticides in Surface Waters of Lake Taihu, China

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ABSTRACT

The residues of organochlorine pesticides (OCPs) in surface waters from Meiliang Bay, Gonghu Bay, and Xukou Bay of Lake Taihu, China, were investigated, and their ecological risks were assessed using the risk quotient method and probabilistic risk assessment. Environmental concentrations of OCPs in surface water of these bays were relatively lower compared with other rivers or lakes in China. Calculation of risk quotient associated with taxonomic groups indicates moderate ecological risks from OCPs for crustaceans and insects in these bays, while the ecological risks were low for fish and negligible for phytoplankton. The ecological risk quotients associated with individual OCPs were lower than 0.01 in these bays, suggesting a negligible risk to aquatic organisms. Ecological risk from α-HCH was relatively lower compared with DDTs, endosulfans, and γ-HCH. The combined ecological risks were evaluated using probabilistic risk assessment for only eight OCPs owing to a lack of available toxicity data for β-HCH and δ-HCH. The percentage of species with the potential to be at risk from mixture of OCPs was lower than the criteria of 5% in each bay, indicating that the combined ecological risks were acceptable.

Key Words: organochlorine pesticides, ecological risk assessment, surface water, Lake Taihu, China.

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INTRODUCTION

Organochlorine pesticides (OCPs) are a large group of persistent organic pollutants and semi-volatile organic compounds that are commonly found in the environment. OCPs have been of increasing concern worldwide owing to their persistence, bioaccumulation, long-range transmission, and toxicity (Quan *et al*. 2003; Wania and Mackay 1999; Wong *et al*. 2005). Nine OCPs—aldrin, dieldrin, endrin, dichlorodiphenyl-trichloroethane (DDT), chlordane, heptachlor, mirex, toxaphene, and hexachlorobenzene—were included in the "dirty dozen" of the Twelfth Stockholm Convention on Persistent Organic Pollutants in 2004 (UNEP 2004). An additional six OCPs, including α-hexachlorocyclohexane, β-hexachlorocyclohexane, chlordecone, technical endosulfan and its related isomers, lindane, and pentachlorobenzene, were included in the list of persistent organic pollutants at the fourth meeting of the Stockholm Conference of the Parties held May 4–8, 2009 (UNEP 2009). OCPs may enter into aquatic environments through atmospheric precipitation, agricultural runoff, and soil percolation.

Recently, OCP residues in water have frequently been detected worldwide, even in Antarctica and arctic zones (Chiuchiolo *et al*. 2004; Leong *et al*. 2007; Li and Macdonald 2005; Moore *et al*. 2007; Vryzas *et al*. 2009). Furthermore, elevated concentrations of OCPs have been observed in fish, mussels, and birds (Kunisue *et al*. 2003; Monirith *et al*. 2003). These OCPs may have toxic effects on several non-target aquatic organisms, and even on aquatic ecosystems. Previous studies have reported that dietary exposure to OCPs led to reduced survival rates in fish at multiple life stages, including early life, the juvenile and adult stages (Barber *et al*. 2007; Beckvar *et al*. 2005; Milston *et al*. 2003; Papoulias *et al*. 2003). Exposure to DDTs may affect behavior and disrupt the endocrine and immune systems in fish (Barber *et al*. 2007; Milston *et al*. 2003; Papoulias *et al*. 2003). Therefore, it is necessary and imperative to investigate the occurrence of these compounds in aquatic environments and their ecological risks to aquatic ecosystems.

China is one of the largest producers and users of pesticides in the world (Wong *et al*. 2005). Indeed, approximately 203,000 to 381,000 tons of technical-grade pesticides were produced annually in China between 1985 and 1996 (Huang *et al*. 2000), and about 4.9 and 0.4 million tons of DDTs and HCHs were produced in China from the 1950s to the 1980s, accounting for 33% and 20% of total world production, respectively (Hua and Shan 1996). In spite of a ban and restriction on the usage of HCHs in 1983, about 3200 tons of lindane (90% γ-HCH) were used from 1991 to 2000 (Qiu *et al*. 2004; Zhang and Dong 2002). OCPs are also still used in other applications. For example, DDTs are used as raw material for the synthesis of dicofol (Qiu *et al*. 2005). Additionally, DDT-containing anti-fouling paints used for ships is another important source of DDTs in aquatic environments (Lin *et al*. 2009). Overall, OCPs contamination in the aquatic environment is one of the most serious environmental problems in China.

Lake Taihu, which is the third largest freshwater lake in China, is situated in the lower reaches of the Yangtze River, with an area of 2,338 km^2 and an average depth of 1.9 m. Owing to economic development and urbanization in the regions surrounding Lake Taihu, increasing amounts of industrial, agricultural, and municipal wastewaters have been discharged into the lake, which has resulted in changes in

water quality and the ecology of Lake Taihu. In recent years, most studies have focused on eutrophication in Lake Taihu, which seems to arise from high concentrations of nutrients and phosphorus in wastewater discharged from surrounding regions. However, little information is available regarding OCP contamination in surface water and sediment of Lake Taihu (Ta *et al*. 2006; Wang *et al*. 2003), and ecological risks from OCPs in surface waters of Lake Taihu to aquatic organisms are largely unknown, especially with respect to the risks posed to different taxonomic groups. Accordingly, to protect the aquatic ecosystem of Lake Taihu, it is highly desirable to understand the concentrations and distribution of OCPs in water, as well as their subsequent ecological risks to aquatic organisms.

Ecological risk assessment can estimate the likelihood that undesired effects might occur or are occurring as a result of exposure to one or more stressors (USEPA 1998). The traditional approach for ecological risk assessment is a deterministic method or a point risk estimate, such as the risk quotient (RQ) method, which is used for screening level risk characterization. However, deterministic risk assessment cannot quantify the probability and magnitude of ecological effects. As an alternative approach, probabilistic risk assessment (PRA) can quantify ecological risk to aquatic organisms. For example, potentially affected fraction of species, related to the "forward" use of species sensitivity distributions, can provide a more reliable evaluation of the likelihood of potential adverse effects of a compound on aquatic ecosystems.

This study was conducted to determine the OCP residues in surface waters from Meiliang Bay, Gonghu Bay, and Xukou Bay of Lake Taihu, and to assess the ecological risks these OCPs posed to aquatic organisms using two risk assessment approaches, the RQ method and potentially affected fraction of species. The results from this study should be of great value in the risk control of OCPs in Lake Taihu, as well as in ensuring the water safety for residents of areas surrounding Lake Taihu.

METHODS AND MATERIALS

Samples and Sample Analysis

A total of 33 surface water samples were collected from Meiliang Bay, Gonghu Bay, and Xukou Bay of Lake Taihu with the aid of the Global Position System in 2009. They included 10 samples from Meiliang Bay, 11 from Gonghu Bay, and 12 from Xukou Bay. The sampling locations are shown in Figure 1. Water samples were collected using a custom-made stainless steel sampling device and stored in precleaned amber glass bottles in triplicate. The triplicate samples were used for back-up purpose. The samples were filtered through 0.45-μm glass micro-fiber membranes to remove sand and debris after returning to the laboratory within 24 h. The water samples were then stored in the dark at between 0°C and 4°C prior to extraction. These samples were subsequently analyzed for 10 OCPs: α-HCH, β-HCH, δ-HCH, γ-HCH, 4,4-DDT, 4,4-DDD, 4,4-DDE, α-endosulfan, β-endosulfan, and endosulfan sulfate.

Surrogates (decachlorobiphenyl) were then added to the water samples, and they were subsequently extracted using a solid-phase extraction (SPE) system (Supelclean LC-18) according to the procedures published by Zhou *et al*. (2007). The

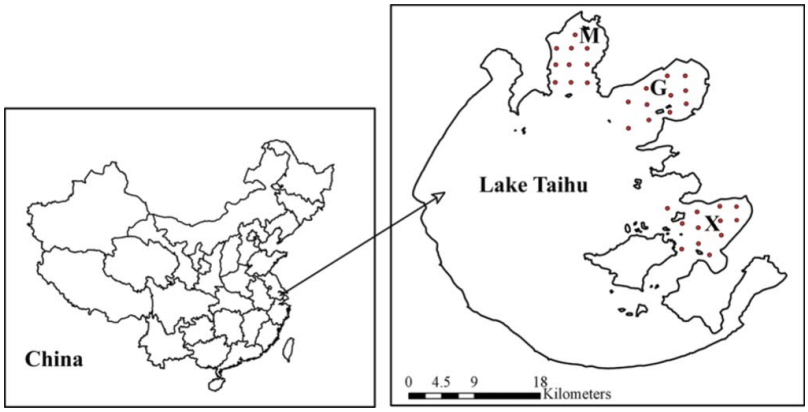

Figure 1. Sampling sites in Meiliang Bay (M), Gonghu Bay (G), and Xukou Bay (X) of Lake Taihu. (Color figure available online.)

SPE cartridges were activated with 10 mL of dichloromethane and then washed with 10 mL of methanol and 10 mL of ultra-pure water prior to extraction. Next, water samples (1 liter) were passed through the cartridges at a flow rate of 5 mL/min under a vacuum pump. After extraction, the cartridges were eluted with 6 mL dichloromethane and then combined with dichloromethane rinse from the extraction glassware. Residual water was removed from the extraction by anhydrous sodium sulfate (roasted at 300°C) and the volume of the extracts was reduced to 0.1 mL by the rotary evaporator. Finally, internal standards (pentachloronitrobenzene) were added to the samples and they were subjected to GC-ECD analysis (Sun *et al*. 2010). OCPs were analyzed using an Agilent 6890 gas chromatograph (GC) with a ^{63}Ni electron capture detector (ECD). Separation was carried out using a HP-5 capillary column (30 m × 0.25 mm × 0.25 μm). The column temperature program was as follows: initial temperature of 60°C (hold for 1 min), which was increased to 200°C at a rate of 6°C/min, then to 210°C/min at a rate of 1°C/min and finally to 290°C at a rate of 10°C/min, where it was held for 10 min. The helium carrier gas flow was maintained at 1.0 mL/min. A total of 1 μL of each sample was injected in splitless mode. The injector temperature and the ECD temperature were maintained at 250°C and 315°C, respectively.

All analytical procedures were conducted under strict quality control guidelines. For each batch of 10 samples, a procedural blank, a spiked blank, a spiked matrix sample, and a duplicate spiked matrix sample were processed to check for interference and cross-contamination. None of the target compounds were detected in the procedural blanks. The recoveries for OCPs ranged from 82.5% to 104.6%, with the relative standard deviation values ranging from 3.6% to 11.3%. In addition, field blanks (pure water was taken to the field when samples were collected and returned to the laboratory, and then extracted and analyzed in the same manner as the water samples) were analyzed to evaluate the effects of sampling methodology and laboratory procedures on the concentrations of OCPs in the water samples.

Ecological Risk Assessment Methods

Risk quotient based on predicted no-effect concentration

RQ of individual OCPs was calculated using the following equation:

$$\mathrm{RQ} = \mathrm{EC}/\mathrm{PNEC} \tag{1}$$

where EC is the environmental concentration of individuals OCPs, and PNEC is the predicted no-effect concentration of OCPs to aquatic organisms.

The acute toxicity data (LC50: median lethal concentration/EC50: median effect concentration) and an assessment factor (AF) were used to determine the PNEC as follows:

$$\mathrm{PNEC} = \mathrm{LC50\,or\,EC50}/\mathrm{AF} \tag{2}$$

Toxicity data were obtained from the Pesticide Action Network's Pesticide Database (www.pesticideinfo.org). The toxicity data were only selected when their endpoints were clearly related to changes in the population structure such as growth, reproduction, and survival. For acute toxicity data, a conservative AF was set at 100 (Van de Meent *et al*. 1990) in this study.

The sum of RQ for all the detected OCPs was calculated to estimate the total toxicity to each taxonomic group. The RQ addition method was based on the assumption that toxicities are additive or approximately additive, and the synergistic, antagonistic, or other interactions between OCPs were not considered. When the values of $\mathrm{RQ} \geq 1$, a high risk is expected, while the values of $0.1 \leq \mathrm{RQ} < 1$ indicate a medium risk and the values of $0.01 \leq \mathrm{RQ} < 0.1$ indicate a low risk (Sanchez-Bayo *et al*. 2002).

The relative contribution (RC) of individual OCPs to the total ecological risk was calculated using the following equation:

$$\mathrm{RC}(\%) = (\mathrm{RQ_i} \times 100)\big/RQ_m \tag{3}$$

where RQ_i is the risk quotient of individual OCP i and RQ_m is the sum of risk quotients of individual OCPs.

Probabilistic risk assessment

The method described by Van Straalen and Dennenman (1989) was used to derive the environmental criteria based on the assumption that the toxicity data of different species followed a log-logistic distribution. The mean and standard deviation of the ln-transformed toxicity data were used to describe the probabilistic distribution of these data. The hazardous concentration for 5% of the species (HC5) can be estimated from the log-logistic distribution using the following equation:

$$\mathrm{HC5} = exp\,(x_m - k_L s_m) \tag{4}$$

where m is the number of the test species; x_m and s_m represent the mean and standard deviation of the ln-transformed toxicity data, respectively; k_L is the extrapolation constant at the 50% confidence level, k_L were 1.81, 1.65, 1.64, 1.70, 1.85, 1.65, 1.65, and 1.85 for α-HCH, γ-HCH, 4, 4-DDT, 4, 4-DDD, 4, 4-DDE, α-endosulfan, β-endosulfan, and endosulfan sulphate, respectively (Kooijman 1987).

The ecological risks of the individual OCPs to the aquatic ecosystem were estimated using potentially affected fraction of species (*i.e.,* the inverse method described by Van Straalen and Denneman 1989). The ecological risk can be characterized as the probability (Φ) that the species in the aquatic ecosystem may be affected by a given environmental exposure concentration (c) using the following equation:

$$\Phi = [1 + exp((x_m - \ln c)/(k_L \times s_m/\ln(95/5)))]^{-1} \quad (5)$$

The combined ecological risk of the mixtures of OCPs can be estimated using the addition of probabilities of individual OCPs as follows:

$$\Phi[A_1 + A_2 + \cdots + A_n] = \sum_{i=1}^{n} \Phi[A_i] - \sum_{i1<i2} \Phi[A_{i1}A_{i2}] + \cdots + (-1)^{r+1} \sum_{i1<i2<i3} \Phi[A_{i1}A_{i2}\ldots A_{ir}] + \cdots + (-1)^{n+1}\Phi[A_1A_2\ldots A_n] \quad (6)$$

where A_i represents OCP i. The summation $\sum \Phi[A_{i1}A_{i2}\ldots A_{ir}]$ is taken over all of the $\binom{n}{r}$ possible subsets of the size r of the set $\{1, 2, \ldots, n\}$. This equation does not account for synergistic or antagonistic interactions between OCPs.

Risk quotient based on hazardous concentration for 5% of the species

Based on the hazardous concentration for 5% of the species, ecological risks posed by individual OCPs to the aquatic ecosystem can be defined as the ecological risk quotient (ERQ) (EC 1996), which can be calculated using the following equation:

$$\text{ERQ} = \text{EC}/(\text{HC5}/\text{SF}) \quad (7)$$

where EC is the environmental concentration of individual OCPs, and the HC5 value is calculated using the method mentioned above. The safety factor (SF) was set at 5 in this study (EC 1996).

RESULTS AND DISCUSSION

Environmental Concentrations of OCPs

Ten individual OCPs were detected in Meiliang Bay, Gonghu Bay, and Xukou Bay of Lake Taihu: α-HCH, β-HCH, δ-HCH, γ-HCH, 4,4-DDT, 4,4-DDD, 4,4-DDE, α-endosulfan, β-endosulfan, and endosulfan sulfate. A statistical summary of OCP concentrations in the surface water of these three bays is shown in Table 1. The average environmental concentrations of the total OCPs were 2.34, 1.41, and 1.65 ng/L in Meiliang Bay, Gonghu Bay, and Xukou Bay, respectively. The average environmental concentrations of DDTs were 0.37, 0.23, and 0.20 ng/L in Meiliang Bay, Gonghu Bay, and Xukou Bay, respectively, which were less than the environmental quality standard for surface water (GB3838-200) (<2000 ng/L for DDTs) (SEPA 2002). The average environmental concentrations of γ-HCH were 0.23, 0.24, and 0.50 ng/L in Meiliang Bay, Gonghu Bay, and Xukou Bay, respectively, which were

Table 1. Concentrations (ng/L) of OCPs in surface water of the three bays of Lake Taihu.

	Meiliang Bay				Gonghu Bay				Xukou Bay			
OCPs	Min	Max	M	SD	Min	Max	M	SD	Min	Max	M	SD
α-HCH	0.28	1.93	0.87	0.63	0.18	0.67	0.35	0.15	0.20	0.55	0.34	0.10
β-HCH	0.16	0.69	0.45	0.16	0.20	0.49	0.32	0.09	0.10	0.47	0.21	0.10
δ-HCH	nd	0.44	0.13	0.14	nd	0.13	0.03	0.03	nd	0.12	0.04	0.04
γ-HCH	0.15	0.46	0.23	0.09	0.14	0.34	0.24	0.06	0.24	0.72	0.50	0.17
HCHs	0.73	3.34	1.68	0.93	0.66	1.39	0.94	0.21	0.59	1.59	1.09	0.31
4,4-DDT	nd	0.11	0.04	0.03	nd	0.10	0.05	0.03	nd	0.48	0.07	0.13
4,4-DDD	0.06	0.43	0.12	0.11	0.03	0.08	0.05	0.17	0.02	0.07	0.05	0.01
4,4-DDE	0.13	0.43	0.21	0.09	0.09	0.18	0.13	0.03	0.05	0.10	0.08	0.02
DDTs	0.21	0.93	0.37	0.22	0.13	0.31	0.23	0.06	0.10	0.58	0.20	0.13
α-Endosulfan	0.02	0.17	0.05	0.04	0.03	0.06	0.03	0.02	0.04	0.09	0.06	0.02
β-Endosulfan	nd	0.06	0.02	0.01	nd	0.05	0.03	0.005	nd	0.04	0.02	0.009
Endosulfan sulphate	nd	0.47	0.22	0.16	0.13	0.28	0.18	0.06	nd	0.61	0.28	0.16
Endosulfans	0.05	0.52	0.29	0.16	0.16	0.35	0.24	0.07	0.07	0.68	0.36	0.17
Total OCPs	1.13	2.58	2.34	1.18	1.17	1.84	1.41	0.19	0.89	2.47	1.65	0.44

M: mean; SD: standard deviation; nd: not detected.

less than the criteria value of <1000 ng/L set by the State Environment Protection Agency of China (SEPA 2002).

To understand the current contamination status of OCPs in the study areas, the concentrations of OCPs measured in surface water of Lake Taihu were compared with the results from other surface waters (Table 2). As seen in Table 2, the concentrations of individual OCPs in Lake Taihu (this study) were lower than those reported in Minjiang River (Zhang *et al*. 2003), Qiantang River (Zhou *et al*. 2006), Tonghui River (Zhang *et al*. 2004), Lake Xihu (Liang *et al*. 2008), Jiulongjiang River (Zhang *et al*. 2001), Liaohe River (Zhang *et al*. 2002), Daliaohe River (Li *et al*. 2009), Suzhouhe River (Hu *et al*. 2005), Pearl River (Yang *et al*. 2004), Yangtze River (Tang *et al*. 2008), Haihe River (Wang *et al*. 2007), and Guangting Reservoir-Yongding River (Kang *et al*. 2003) in China. The average concentrations of γ-HCH and DDTs were found to be lower in Lake Taihu in this study than the previous study conducted by Ta *et al*. (2006). When compared with rivers or lakes of other countries, the concentrations of individual OCPs from Lake Taihu (this study) were higher than those in the Nestos River of Greece (Golfinopoulos *et al*. 2003) but lower than those in the Kucuk Menderes of Turkey (Turgut 2003) and the Ebro River of Spain (Claver *et al*. 2006). This may be related to the less current use of OCPs in the areas surrounding Lake Taihu. In addition, the eutrophication in Lake Taihu may contribute to lower concentrations of OCPs in surface water compared with other rivers, because eutrophication may cause dilution of contaminants in increasing amounts of biomass, increased contaminant scavenging by dissolved organic carbon (DOC), and increased sedimentation of contaminants (Gunnarsson *et al*. 1995; Taylor *et al*. 1996; Koelmans *et al*. 2001).

Table 2. Concentrations of OCPs (ng/L) in surface water of rivers and lakes worldwide (standard deviations are in parentheses).

Water body	n	α-HCH	β-HCH	γ-HCH	δ-HCH	4,4-DDT	4,4-DDD	4,4-DDE	α-endosulfan	β-endosulfan	Endosulfan sulphate	Reference
Minjiang River	9	46.41(39.42)	92.50(54.63)	19.02(10.95)	47.57(28.29)	33.63(12.98)	16.92(12.07)	91.46(43.24)	31.25(17.64)	77.24(51.79)	42.08(33.11)	(Zhang *et al.* 2003)
Qiantang River	45	3.62(4.84)	2.4(6.67)	18.06(16.38)	3.48(4.36)	1.34(2.04)	0.78(1.01)	2.20(4.34)	nr	nr	nr	(Zhou *et al.* 2006)
Tonghui River	16	137.23(137.06)	56.98(104.61)	25.13(11.40)	137.03(117.23)	61.63(97.45)	4.41(9.60)	25.78(49.26)	13.75(37.55)	67.02(130.31)	nd	(Zhang *et al.* 2004)
Lake Xihu	7	8.19(4.83)	29.72(27.69)	4.70(8.43)	3.59(4.35)	0.39(0.72)	0.28(0.52)	1.93(2.69)	0.10(0.26)	nr	nr	(Liang *et al.* 2008)
Jiulong Jiang River	19	2.52(4.79)	44.74(35.08)	2.41(2.30)	29.54(62.62)	0.86(2.47)	1.82(3.18)	11.58(14.41)	1.65(2.09)	126.76(214.99)	194.57(211.76)	(Zhang *et al.* 2001)
Liaohe River	4	7.29(7.09)	4.56(3.21)	2.11(0.96)	nr	0.93(0.66)	0.59(0.41)	1.26(0.90)	nr	nr	nr	(Zhang *et al.* 2002b)
Suzhouhe River	6	11.5(18.8)	13.5(21.2)	16.83(14.54)	1.33(3.27)	20.00(7.97)	19.83(20.92)	35.00(29.92)	8.17(7.03)	7.50(16.05)	15.17(9.87)	(Hu *et al.* 2005)
Pearl River[a]	6	4.10(2.33)	1.78(0.77)	2.44(2.68)	3.49(1.52)	0.16(0.04)	0.16(0.48)	0.26(0.08)	0.09(0.04)	0.10(0.07)	0.01(0.005)	(Yang *et al.* 2004)
Pearl River[b]	6	27.23(24.77)	7.23(4.25)	4.13(3.08)	7.50(5.97)	1.30(0.57)	3.11(0.77)	1.21(0.30)	4.40(2.57)	6.65(9.12)	1.71(0.60)	(Yang *et al.* 2004)
Guangting Reservoir -Yongding River	13	4.24(6.37)	4.12(3.47)	3.01(4.89)	1.57(2.55)	1.49(4.19)	nr	nr	0.19(0.48)	6.10(13.43)	0.05(0.17)	(Kang *et al.* 2003)
Haihe River	21	70.48(97.21)	234.43[c](155.38)	116.67(121.79)	2.76(10.77)	5.10(13.39)	13.00(37.87)	nr	nr	nr	(Wang *et al.* 2007)	
Daliao River	12	5.0 (3.3)	1.6(1.3)	1.9(1.2)	2.2(1.8)	0.7(0.4)	1.1(0.8)	0.3(0.2)	0.7(0.4)	0.3(0.1)	nr	(Li *et al.* 2009)
Wuhan Reach, Yangtze River	30	3.15(2.82)	1.32(3.76)	1.69(1.01)	0.92(4.47)	1.49(3.65)	0.008(0.05)	0.03(0.15)	nr	nr	nr	(Tang *et al.* 2008)
Lake Taihu (Meiliang Bay)	10	nr	nr	1.97(1.54)	nr	1.08(1.94)	0.50(0.70)	0.36(0.47)	nr	nr	nr	(Ta *et al.* 2006)
Nestos River, Greece	12	nd-0.13	nd-0.10	nd-0.08	nd-0.19	nd-0.04	nd	nd-0.06	nd-0.02	nd-0.02	nd-0.06	(Golfinopoulos *et al.* 2003)
Kucuk Menderes, Turkey	nr	nd-40	101–121	nd-398	nd	nd-34	nd-71	nd	nd-23	23–25	120–12.3	(Turgut 2003)
Ebro River, Spain	nr	nd- < 15	nd- < 15	< 15–59	nd-20	nd- < 30	< 30–35	nd-22	nd- < 15	nr	nd- < 15	(Claver *et al.* 2006)
Lake Taihu	33	0.52(0.42)	0.33(0.15)	0.07(0.09)	0.32(0.15)	0.05(0.09)	0.07(0.05)	0.14(0.07)	0.05(0.03)	0.02(0.01)	0.23(0.14)	This study

nd: not detected; nr: not reported; [a]samples in high flow season; [b]samples in low flow season; [c]total concentration of β-HCH and γ-HCH.

Table 3. Lowest acute toxicity data (LC50/EC50) (ng/L) and PNEC for four taxonomic groups.

OCPs	Phytoplankton (EC50)	$PNEC_p$[a]	Crustaceans (EC50)	$PNEC_c$[b]	Insects (LC50)	$PNEC_i$[c]	Fish (EC50)	$PNEC_f$[d]
α-HCH	—	—	398,630	3986.30	—	—	726,630	7266.30
β-HCH	—	—	—		—	—	1,226,470	12,264.70
δ-HCH	—	—	—		—	—	1,081,410	10,814.10
γ-HCH	1,669,730	16,697.30	8620	86.20	4290	4.29	34,350	343.50
4,4-DDT	900,000	9000.00	860	8.60	3300	3.30	13,400	134.00
4,4-DDD	—	—	1290	12.90	27,110	271.10	45,830	458.30
4,4-DDE	—	—	10,990	109.90	3180	31.80	32,000	320.00
α-Endosulfan	13,000	130.00	100	1.00	680	6.80	1270	12.70
β-Endosulfan	13,000	130.00	100	1.00	680	6.80	1270	12.70
Endosulfan sulfate	—	—	444,310	4443.10	1200	12.00	1670	16.70

[a]$PNEC_p$ of OCPs for phytoplankton; [b]$PNEC_c$ of OCPs for crustaceans; [c]$PNEC_i$ of OCPs for insects; [d]$PNEC_f$ of OCPs for fish.

Ecological Risk Assessment

To provide appropriate protection for the aquatic ecosystem of Lake Taihu, the predominant aquatic species in the lake were selected, and the taxonomic groups (phytoplankton, crustaceans, insects, and fish) are treated separately in calculation of RQ for detected OCPs. The lowest toxicity data of individual OCPs for each taxonomic group, coupled with PNEC of individual OCPs for these four taxonomic groups, are presented in Table 3. RQ of individual OCPs were calculated by the environmental concentrations in Table 1 divided by the PNEC listed in Table 3. The sum of RQs of individual OCPs indicated the total ecological risk of OCPs to a certain taxonomic group (Figure 2). The sum of RQs (0.0987) was the highest in

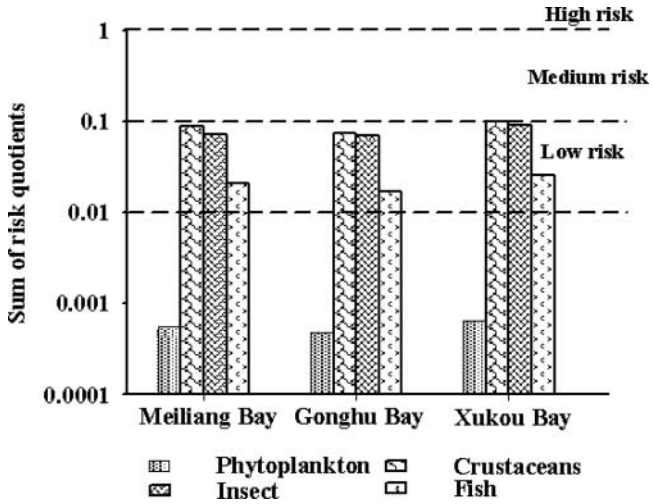

Figure 2. Total ecological risks of OCPs to taxonomic groups in surface water of the three bays of Lake Taihu.

Xukou Bay for crustaceans, while the lowest risk (0.00065) was found in Gonghu Bay for phytoplankton. As seen in Figure 2, the ecological risks were moderate for crustaceans and insects in all of the study bays, while they were low for fish and negligible for phytoplankton. These results are in accordance with those of previous studies that showed that crustaceans and insects are more vulnerable to the OCPs than algae (Brix *et al*. 2001; Steen *et al*. 1999). This may be explained by the fact that the detected OCPs were insecticides that primarily act on the nervous system of organisms by interdicting the neuron conduction procedure. For example, DDTs exert toxicity on organisms by altering Na^+/Ca^{2+} exchange in the sodium channel of the German cockroach (*Blattella germanica*) (Rashatwar and Matsumura 1985) and by inhibiting the activity of Ca^{2+}-Mg^{2+}-ATPase in the peripheral nerves and muscles of lobster (*Homarus americanus*) (Ghiasuddin and Matsumura 1981). The neuron conduction was interrupted by HCHs as a consequence of the accumulation of acetylcholine between the nerve cell as a result of stimulation of the presynaptic membrane (Shankland and Schroeder 1973), or inhibition of the activity of Na^+-K^+-ATPase in the nervous system (Uchida *et al*. 1974). Phytoplankton was not the target organism for the detected OCPs, while photosynthesis, which is an important process in algae, is generally influenced by herbicides.

The relative contributions of individual OCPs to the total ecological risk were calculated to identify the OCPs that posed a higher risk to a certain taxonomic group (Figure 3). As shown in Figure 3, 4,4-DDD, and 4,4-DDE were found to be most toxic for phytoplankton in all three bays of Lake Taihu, while α-endosulfan and β-endosulfan contributed the most to the total risk to crustaceans, and endosulfan sulphate posed the greatest risks to insects and fish. It was clear that DDTs (including 4,4-DDT, 4,4-DDD, and 4,4-DDE) and endosulfans (including α-endosulfan, β-endosulfan, and endosulfan sulphate) made the greatest contribution to the ecological risk based on the toxicity data, and that a much lower contribution to

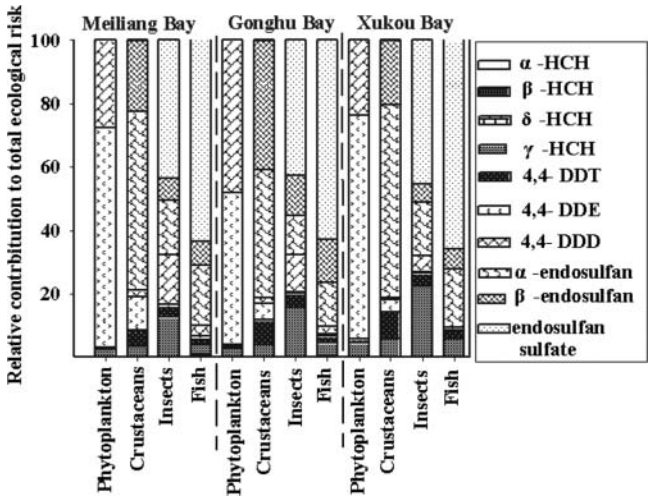

Figure 3. Relative contribution of detected individual OCPs to total ecological risk for taxonomic groups.

Table 4. Summary of HC5 calculations for OCPs in surface waters of Lake Taihu.

		ln (toxicity data) (μg/L)			
OCPs	m	x_m	s_m	r^2	HC5 (μg/L)
α-HCH	6	6.77	0.47	0.953	372.15
γ-HCH	50	4.85	1.62	0.984	8.82
4, 4-DDT	69	4.15	2.96	0.991	0.46
4, 4-DDD	14	3.65	2.73	0.975	0.37
4, 4-DDE	5	3.41	1.71	0.992	1.28
α-Endosulfan	50	1.90	1.75	0.995	0.38
β-Endosulfan	50	1.90	1.75	0.995	0.38
Endosulfan sulphate	5	2.97	2.03	0.879	0.46

ecological risk is posed by α-HCH when compared with γ-HCH owing to the less hazardous effect on the aquatic organisms.

To assess the ecological risk of the individual OCPs using PRA, at least four toxicity data points were necessary to develop the log-logistic distribution (Okkerman *et al*. 1991). For both β-HCH and δ-HCH, only three LC50 values for fish were available; therefore, the ecological risks from both β-HCH and δ-HCH were not further evaluated in this study. The toxicity data were well fitted to a log-logistic distribution at the 5% significance level using a goodness-of-fit test (Table 4). The number of toxicity data points and parameters describing the log-logistic distributions, as well as HC5 values at the 50% level of certainty, are presented in Table 4. When comparing γ-HCH and 4,4-DDT, the scale parameter (s_m) influenced the HC5 values to a great extent. Although the mean value of ln-transformed toxicity data for γ-HCH approximated that of 4,4-DDT, the distribution of 4,4-DDT stretched toward the more sensitive species, resulting in a relatively lower HC5 (0.46 μg/L) when compared with that of γ-HCH (8.82 μg/L).

In addition, the ERQs of individual OCPs to all aquatic organisms were calculated based on HC5 derived from the probabilistic distribution of the toxicity data. The results are shown in Figure 4. The ERQs of individual OCPs were lower than 0.01, indicating a negligible risk to aquatic organisms in the three bays of Lake Taihu. It was clear that α-HCH posed considerably lower ecological risk compared with DDTs (including 4,4-DDT, 4,4-DDD, and 4,4-DDE), endosulfans (including α-endosulfan, β-endosulfan and endosulfan sulphate), and γ-HCH due to less hazardous effect on the aquatic organisms. The usage of endosulfans were banned in some developed countries, but they were still extensively used in China due to their low cost and high effectiveness (Siang *et al*. 2007). Although DDTs have been prohibited from being produced and used, high DDTs levels in commercial dicofol and DDT-containing anti-fouling paints contributed to the high concentrations of DDTs in the environment (Lin *et al*. 2009; Qiu *et al*. 2005). Extensive usage of lindane (90% γ-HCH) coupled with the most hazardous effect on the aquatic organisms lead to the considerably higher ecological risk compared with other HCHs. Therefore, more attention should be paid to the ecological risks from DDTs, endosulfans, and γ-HCH. It should be noted that although the environmental concentrations of DDTs in surface water

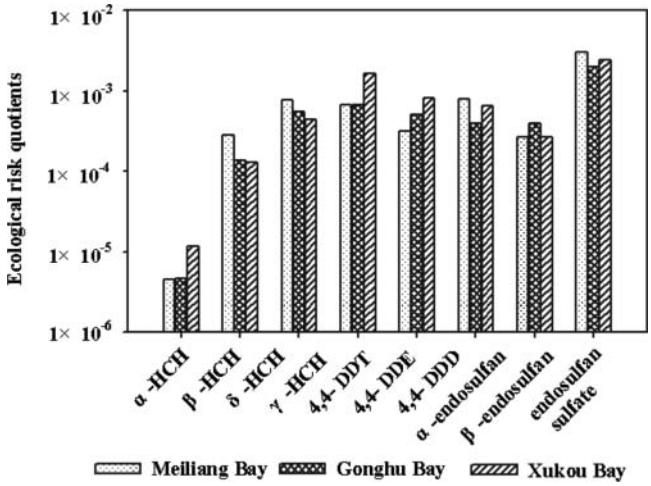

Figure 4. Ecological risk quotients (ERQs) of individual OCPs to all aquatic organisms based on HC5 values.

of Lake Taihu were slightly lower than those of HCHs, their ecological risks were significantly higher than those from HCHs, which can be ascribed to higher toxic effects of DDTs on the aquatic organisms. The ecological risks from OCPs calculated in this study were considerably lower than those from organophosphorus pesticides showed in previous studies (Qu *et al*. 2010), which indicated that ecological risks to aquatic organisms were mainly dominated by organophosphorus pesticides in the surface water of Lake Taihu.

In reality, aquatic organisms in the environment are simultaneously exposed to mixtures of various chemicals rather than single chemicals, but the exposures to multiple chemicals are often treated as individual events in many cases. Ecological risk therefore has been estimated only for individual chemicals and the combined risk of simultaneous exposure to a mixture of chemicals was not considered, which resulted in underestimation of the ecological risks from actual environmental exposure concentrations. Therefore, it is necessary to evaluate the combined ecological risk from mixture of OCPs in Lake Taihu, and the combined ecological risk of OCPs listed in Table 3 is depicted in Figure 5. As shown in Figure 5, the percentages of species that can be at risk were found to be 0.59%, 0.41%, and 0.65% for Meiliang Bay, Gonghu Bay and Xukou Bay, respectively. The risk level from mixtures of OCPs in the three bays were lower than the criteria of 5% set by the Dutch National Institute of Public Health and the Environment and the U.S. Environmental Protection Agency (USEPA) (DGM 1989; Stephen *et al*. 1985). These data indicates that the highest risk posed by mixtures of OCPs was found in Xukou Bay, followed by Meiliang Bay and Gonghu Bay. However, it is worth noting that these ecological risks were calculated based on the data for only eight OCPs owing to a lack of available toxicity data for β-HCH and δ-HCH. A more comprehensive assessment of ecological risks posed by pesticides including insecticides and herbicides should be conducted in the future.

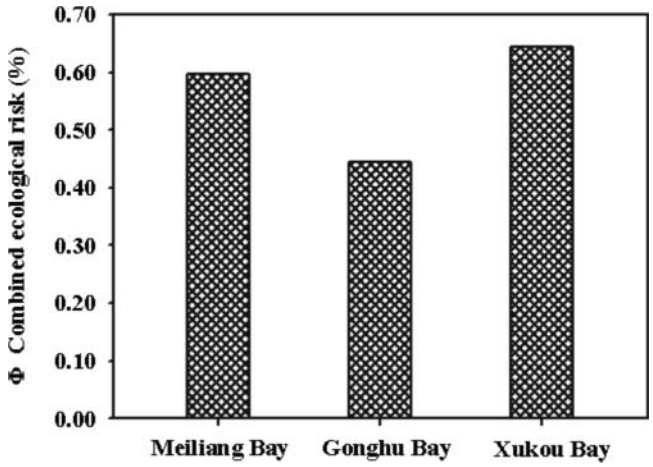

Figure 5. Combined ecological risk of mixtures of OCPs in surface waters of the three bays of Lake Taihu.

CONCLUSIONS

Comprehensive surveys of OCPs in surface waters of Meiliang Bay, Gonghu Bay, and Xukou Bay in Lake Taihu were conducted, and the ecological risks of individual and mixtures of OCPs were then evaluated. The average environmental concentrations of total OCPs were 2.34, 1.41, and 1.65 ng/L in Meiliang Bay, Gonghu Bay, and Xukou Bay, respectively. Relatively lower concentrations of OCPs were observed in the three bays of Lake Taihu when compared with other rivers or lakes in China. RQ calculation based on toxicity data indicated that the mixtures of OCPs posed a moderate risk for crustaceans and insects, while they posed a low risk for fish and negligible risk for phytoplankton. The ERQs based on HC5 imply that endosulfan sulphate posed the highest ecological risk to the aquatic ecosystem of Lake Taihu, whereas α-HCH posed the lowest ecological risk. The combined ecological risk of mixtures of OCPs (not including β-HCH and δ-HCH) to the aquatic organisms in descending order was as follows: Xukou Bay (0.65%), Meiliang Bay (0.59%), and Gonghu Bay (0.41%). The percentages of species that could be at risk did not exceed the acceptable level of 5%, indicating an acceptable risk level (DGM 1989; Stephen *et al*. 1985). A more complete risk assessment should be conducted based on a more complete set of toxicity data and a wider series of environmental exposure concentrations. In addition, ecological risks from other chemicals detected in water samples of Lake Taihu should be taken into consideration in future studies.

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