Aquatic biota as potential biological indicators of the contamination, bioaccumulation and health risks caused by organochlorine pesticides in a large, shallow Chinese lake (Lake Chaohu)

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Abstract

Aquatic biota have long been recognized as bioindicators of the contamination caused by hydrophobic organic contaminants (HOCs) in aquatic environments. The primary purpose of the present study is to identify which species of aquatic biota are the most sensitive to organochlorine pesticides (OCPs) in Lake Chaohu and can therefore serve as indicators of the lake's health and assist in the assessment of OCPs risks to human health. OCP levels in eight species of aquatic biota were measured using GC–MS, and the relationships between the biota and OCP levels in the water and suspended solids were studied. DDTs pose potential human health risks and were the predominant OCP components found in the aquatic biota. DDT had the highest mean bioaccumulation factor (BAF) and biota suspended solids accumulation factor (BSSAF) of all of the studied OCP components. The food web magnification factors (FWMF) for p,p'-DDT were greater than 1, implying that biomagnification occurred. This finding indicates that DDTs still pose a serious threat to the ecosystem and human health in Lake Chaohu, even though the agricultural application of DDT powder has been officially banned since 1983. There were significant positive relationships between OCPs levels in Culter erythropterus and those in both water and suspended solids, as well as between OCPs levels in Protosalanx hyalocranius and those in suspended solids. This finding suggests that C. erythropterus and P. hyalocranius are the most sensitive aquatic biota to OCPs and may serve as the most effective bioindicators for monitoring OCP contamination in the water and suspended solids of Lake Chaohu. Megalobrama amblycephala, which contained the highest wet weight mean OCP concentration, is the most sensitive OCP indicator and can be used to assess the human carcinogenic risk of OCPs in Lake Chaohu.

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1. Introduction

Aquatic biota are frequently used as biological indicators to monitor the levels of Persistent Organic Pollutants (POPs) in aquatic environments (van der Oost et al., 2003; Lanfranchi et al., 2006; Guo et al., 2008; Zhao et al., 2013; Lacorte et al., 2006; Jaspera et al., 2013), to analyze POP bioaccumulation (Haruhiko et al., 2003; Arnot and Gobas, 2006; van Leeuwen et al., 2008; Coat et al., 2011) and biomagnification in the food chain (Hu et al., 2010; Zhang et al., 2013; Villa et al., 2011; Li et al., 2008b), and to evaluate human health risks associated with the consumption of contaminated water products (Dong et al., 2006; Cheung et al., 2007; Dennis, 2007; Yu et al., 2011; Zhou et al., 2008; Li et al., 2008a). Organochlorine pesticides (OCPs) are a category of POPs that have aroused widespread concern due to their high carcinogenicity and their persistence, semi-volatility, effects on wildlife and ability to bioaccumulate (Willett et al., 1998; Wu et al., 1999; Zhou et al., 2001). The production and use of sixteen types of OCPs, including dichloro-diphenyl-trichloroethane (DDT), chlordane, mirex, aldrin, dieldrin, endrin, hexachlorobenzene, heptachlor, toxaphene, α-hexachlorocyclohexane (α-HCH), β-HCH, lindane (γ-HCH), chlороdecone (kepone), pentachlorobenzene and endosulfan, have been prohibited by the Stockholm Convention on Persistent Organic Pollutants (UNEP, 2001, 2011). In China, the agricultural application of DDT and HCH has been banned since 1983, while the production, transport, use, and import/export of DDT, chlordane, mirex, and hexachlorobenzene (HCB) have been forbidden since May 2009 (MEP, 2009). However, some industrial
products, such as lindane (which is 99% gamma-HCH) and dicofol (which contains DDT analogs that form as manufacturing impurities), are still used in some regions of China (Qiu et al., 2005), and DDT is also used as a secondary material in antifouling paint for ships (Yu et al., 2011). As a result, OCPs have continued to be detected in water and aquatic biota throughout China in recent years (Li et al., 2007; Guo et al., 2008; Tao et al., 2005, 2008; He et al., 2012; Xu et al., 2013; Ouyang et al., 2012, 2013, 2014). While extensive studies on the occurrence of OCPs in water and aquatic biota have been performed (Hoeckstra et al., 2003; Skarpheidsindottir et al., 2010; Wang et al., 2014; Zhou et al., 2008; Goutner et al., 2012; Liu et al., 2012; He et al., 2014), little research into the bioaccumulation and biomagnification of OCPs in relation to suspended solids exists; and little is known about the influence of particulate OCPs other than dissolved OCPs on aquatic biota in freshwater ecosystems (Hendriks et al., 1998; Burkhard and Lukasewycz, 2000; He et al., 2014). Yet, suspended solids may be an important route for the bioaccumulation of OCPs. The biological composition and environmental conditions of aquatic systems may differ from one another, which may result in variations in biotic sensitivity to OCPs from ecosystem to ecosystem. Therefore, it is necessary to identify which species of aquatic biota are the most sensitive bioindicators for monitoring OCP contamination and the associated ecological effects of OCPs in specific aquatic ecosystems.

Lake Chaohu, which is located in the heart of Anhui Province (31°25′28″–31°43′28″ N, 117°16′54″–117°51′46″ E), is the fifth-largest freshwater lake in China and is approximately 760 km². In addition to fishing and its use in agricultural irrigation, Lake Chaohu is source of drinking water for the 9.6 million residents in the surrounding areas; and the water quality directly affects the health and safety of the residents. Before OCPs were banned, each environmental medium within Lake Chaohu was contaminated by long-term and extensive agricultural activities (Li et al., 2010; Ouyang et al., 2013). The growing amount of industrial and domestic wastewater discharged into the lake has further exacerbated the situation. Previous studies of Lake Chaohu have shown that OCP contamination remains in various media, including the water, suspended solids, sediment, the air and dust fall (He et al., 2012; Wang et al., 2012; Liu et al., 2013; Ouyang et al., 2012, 2013, 2014). However, limited information has been reported on the relationship between OCPs in aquatic biota and those in the water and suspended solids, as well as on the bioaccumulation, biomagnification and health risks of OCPs. The objectives of this study are to (1) investigate residual levels of OCPs in aquatic biota and identify the relationships between those levels and OCPs in the water and suspended solids; (2) analyze the relationships between OCP bioaccumulation and concentrations in suspended sediments and dissolved in water; (3) assess the potential health risks associated with the consumption of aquatic biota; and (4) identify the species of aquatic biota that are the most sensitive to OCPs and can serve as bioindicators for monitoring the contamination and associated risks of OCPs in the water and suspended solids of Lake Chaohu.

2. Materials and methods

2.1. Sample collection

In January 2011, a fisherman was employed to catch aquatic biota throughout the lake. Different sizes of six species of commonly consumed freshwater fishes, one species of shrimp (Leander modestus Heller) and one species of snail (Cipangopaludina chinensis) were collected. The six fish species were spotted steed (Hemibarbus maculates), carp (Cyprinus carpio), topmouth culter (Culter erythrophleus), blunt snout bream (Megalobrama amblycephala), large icefish (Protosalanx hyalocranius), and bighead carp (Aristichthys nobilis). The fish were caught and stored in polypropylene boxes filled with lake water. To reduce individual differences, the muscles on both dorsal flanks and the chests of three or five of the same fish species were combined into one mixed sample, and a total of three parallel samples were taken for each fish species. After the wet weight was obtained, the samples were freeze-dried (FDU-830, Tokyo Kasei Kogyo Co., Japan), weighed to measure dry weight and ground into a granular powder with a ball mill (MM400, Retsch GmbH, Germany). Amber glass bottles were used to hold the sample powder and sealed into a dryer until analyzed. The physical characteristics of the investigated species are presented in Table S1 of Appendix A.

Water and suspended solids data for Lake Chaohu were collected and published in two previous studies (Liu et al., 2013; Ouyang et al., 2013). Water samples were collected from May 2010 to April 2011, and the distribution of sampling sites is shown in Figure S1. The sampling methods used in those studies are as follows (Liu et al., 2013; Ouyang et al., 2013): One liter aliquot of each total water sample was filtered through a 0.45 μm glass fiber filter (ashed at 450°C for 4 h) using a peristaltic pump (80EL005; Millipore Co., USA) and a 142 mm diameter filter plate to separate suspended solids out. Before use, the glass fiber filters were dried and weighed to a constant weight for 24 h. After air-drying, the suspended solid samples were stored in aluminum foil in desiccators to maintain a constant weight. The weight difference between the filters before and after filtering established the weight of the suspended solids. A total of three comparable samples for water and suspended solids were produced for each sampling site. Phytoplankton were collected using 1 L or 2 L water samples concentrated to approximately 50 mL using a 400 mesh plankton net (mesh diameter of 37 μm) and held in 100 mL vials to perform a stable N isotope analysis.

2.2. Extraction and cleanup

Two-gram powder samples were weighed into an extraction tube, and a recovery indicator and internal standard were added. After microwave extraction, the extracts were pressure filtered and concentrated to approximately 1 mL by rotary evaporation. 10 mL of ethyl acetate were added to the extracts, which were then concentrated to 1 mL. The samples were filtered through a 0.45-μm filter and subsequently transferred to GPC vials. After adding 3 mL of ethyl acetate, the samples were cleaned using a GPC instrument (GPC800+, Lab Tech Ltd., China) with a Bio Beads SX-3 column (300 mm × 20 mm, Bio-Rad Laboratories, Inc., USA); A ratio of 1:1 ethyl acetate/hexane was used at a flow of 5 mL/min. The injection volume was 2 mL. Lipids were also extracted by GPC and collected before the target OCPs. Lipid content was collected from 2 to 10 min and stored in a weighed eggplant-shaped flask. Fractions collected at 10–22 min were the target compounds. These extracts were concentrated to approximately 1 mL by rotary evaporation and then re-concentrated to 1 mL after 10 mL of hexane was added. Subsequently, each concentrate sample was loaded into a silica gel SPE cartridge (6 mL, 500 mg, Supelco Co., USA). These cartridges were conditioned with 10–15 mL of hexane before use. After loading, the cartridge was eluted by hexane (two times, 5 mL per elution) and a mixed solution of dichloromethane and hexane (V/V = 1:1, four times, 5 mL per elution). The extracts were concentrated to 1 mL, pentachloronitrobenzene (PCNB, 100 ng, AccuStandard, Inc.) was added to the sample as an internal standard, and the samples were transferred to vials and sealed for analysis.

The extraction and cleanup methods for water and suspended solids samples are presented in Appendix A and our previous papers (Liu et al., 2013; Ouyang et al., 2013). The algae samples were freeze-dried and sealed into a dryer until analyzed.
2.3. Sample analysis and quality assurance

The samples were analyzed using Agilent 6890 gas chromatography and a 5973C mass spectrometer detector with a HP-5 MS fused silica capillary column (30 m × 0.25 mm × 0.25 μm). Helium was used as the carrier gas and applied at a rate of 1 mL/min. The samples (1 μL) were injected using an autosampler in splitless mode at a temperature of 220 °C. The column temperature program was as follows: 50 °C for 2 min, 10 °C/min increase to 150 °C, 3 °C/min increase to 240 °C, 240 °C for 5 min, 10 °C/min increase to 300 °C and 300 °C for 5 min. The ion source temperature of the mass spectrometer was 200 °C; the temperature of the transfer line was 250 °C; and the temperature of the quadrupole was 150 °C. The compounds were quantified in the selected ion mode, and the calibration curve was quantified using the internal standard (PCNB). Three comparable samples of each species were analyzed. Method and procedure blanks were prepared to check for contamination of the solvents and glassware. All samples were extracted and analyzed in duplicate, and there were no detectable OCPs over the limit of quantification in any of the blanks. The recovery test and the detection limit (DL) of the method were performed before sample analysis. Six replicates of a mixed working standard with a concentration of 20 ng/L were used to calibrate the equipment. Analyte recovery ranged from 91.7% to 117.7% (see more details in Table S2 in Appendix A). The DLs for endrin, p, p′-DDE, and o, p′-DDT were all 5 ng/g, while the DLs for other OCPs were less than or equal to 1 ng/g.

2.4. Other analysis

The dissolved organic carbon (DOC) content in the water samples and particulate organic carbon (POC) content in the SPM samples were determined using a total organic carbon analyzer (TOC-5000A; Shimadzu Corp., Japan). A small amount of filtered water was used to detect dissolved organic carbon (DOC) and total carbon (TC, sum of dissolved organic carbon and ionized carbon). Small amounts of the suspended solids samples were used to detect particulate organic carbon (POC) content and total organic carbon (TOC) content, respectively. Analytically pure glucose was used to measure the TC standard curve, and analytically pure sodium carbonate was used to measure the IC standard curve.

The lipid fractions were collected in a weighed eggplant-shaped flask. After drying in a rotary evaporator for 24 h to a constant weight, the flask was reweighed. Lipid content was calculated as the weight difference of the flask before lipid collection and after drying.

All samples, including fish and phytoplankton, were prepared using previously reported methods (Fisk et al., 2001; Winemiller et al., 2007) and analyzed for stable isotope ratios (δ15N) using mass spectrometry (Finnigan MAT 253, Thermo Fisher Scientific, Inc., USA). Nitrogen-stable isotope abundances (δ15N) were expressed as a parts-per-thousand (%) deviation from the standard deviation according to the following equation:

\[
\delta^{15}N = \left( \frac{^{15}N/^{14}N_{\text{sample}}}{^{15}N/^{14}N_{\text{standard}}} - 1 \right) \times 10^3
\]

(1)

where \(^{15}N/^{14}N_{\text{sample}}\) is the isotope ratio in the sample and the \(^{15}N/^{14}N_{\text{standard}}\) value is based on N2 gas. The trophic level of each species was calculated using the formula defined by Winemiller et al. (2007):

\[
TL = \left( \frac{\delta^{15}N_{\text{consumer}} - \delta^{15}N_{\text{reference}}}{3.3} \right) + 1
\]

(2)

where \(\delta^{15}N_{\text{reference}}\) is the mean of the phytoplankton samples and 3.3 is an estimated δ15N value that represents the enrichment between consumers and their food.

2.5. Data processing

The total weight of each OCP can be calculated from the GC-MS results, and the concentration data (ng/g) used in this study were the OCP weight divided by the dry weight (dw), wet weight (ww), and lipid weight (lw) of the fish samples. Microsoft Excel 2013 and SPSS 18.0 software were used to organize and analyze the data. The Kolmogorov–Smirnov test was used to estimate data normality. Using this test, we found that the wet weight and lipid-normalized weight OCP data both fit the log-normal distribution. The relationship between the data was determined using Pearson’s test and the Spearman test; when the significance was below 0.05, the linear regression was considered significant. The difference between the BAF and BSSAF values was determined using an independent-samples t test.

3. Results and discussion

3.1. OCP residuals and their relationship with lipid content in aquatic biota

3.1.1. The residual levels of OCPs in aquatic biota

The following eighteen OCP compounds were detected in the aquatic biota samples: HCH isomers (α-, β-, γ- and δ-HCH), hexachlorobenzene (HCB), heptachlor, isodrin, chlordane isomers (α-chlordane and γ-chlordane), endosulfan isomers (endosulfan I and endosulfan II), DDT and its metabolites (o-, p-, p′-DDE, DDT and DDD), and methoxychlor. The statistical characteristics of the OCP concentrations are shown in Table 1. β-HCH, HCB, and p, p′-DDE were detected in all samples. The geometric mean of the residual levels of total OCPs in all aquatic biota was 10.74 ng/g ww, and the arithmetic mean with standard deviation was 17.27 ± 10.17 ng/g ww. The principal pesticides were DDTs (13.51 ± 8.28 ng/g ww), followed by HCB (1.67 ± 1.00 ng/g ww) and HCHs (1.16 ± 0.95 ng/g ww). Compared with HCH and DDT levels identified in other domestic freshwater lakes such as Lake Taihu (Wang et al., 2011), Minjiang Shuiku reservoir (Li et al., 2010), and the Kangshang and Hukou Areas of Poyang Lake (Sun et al., 2010), the HCH and DDT levels identified in Lake Chaohu were lower. The OCP residuals found in this study were of the same magnitude as those found in Guanting reservoir and Lake Gaobeidian, which received treated wastewater from a wastewater treatment plant nearby (Sun et al., 2005; Li et al., 2008a). The Kolmogorov–Smirnov test was used to estimate data normality; and all concentrations were found to follow a normal distribution after the logarithm transformation.

Fig. 1 shows that M. amblycephala has the highest total OCP levels, while P. hyalocranus and L. modestus have the lowest; and the differences in total OCP concentrations are due to differences in DDT concentrations. Of the OCPs, DDT and HCB levels were highest in C. carpio and M. amblycephala, whereas HCH levels were highest in C. erythropterus.

3.1.2. The composition of OCPs in aquatic biota

The composition of total OCPs, HCHs and DDTs in different species and comparisons between these compositions and those found in the water and suspended solids of Lake Chaohu are presented in Fig. 2. Fig. 2(A) shows that DDTs were the dominant OCPs in all aquatic biota, accounting for 62.1% to 98.4% of all OCPs. The second dominant OCPs were HCBs, which ranged from 10% (L. modestus) to 19.5% (P. halocranus) in all species except
The OCP concentrations in aquatic biota from Lake Chaohu (ng/g ww).

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Standard deviation</th>
<th>Median</th>
<th>Maximum</th>
<th>Minimum</th>
<th>Arithmetic mean</th>
<th>Geometric mean</th>
<th>Detection rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-HCH</td>
<td>0.68</td>
<td>0.13</td>
<td>3.05</td>
<td>0.17</td>
<td>0.36</td>
<td>0.34</td>
<td>95.8</td>
</tr>
<tr>
<td>β-HCH</td>
<td>0.56</td>
<td>0.50</td>
<td>1.95</td>
<td>0.0211</td>
<td>0.72</td>
<td>0.63</td>
<td>100.0</td>
</tr>
<tr>
<td>γ-HCH</td>
<td>0.10</td>
<td>0.04</td>
<td>0.47</td>
<td>0.04</td>
<td>0.07</td>
<td>0.35</td>
<td>95.8</td>
</tr>
<tr>
<td>δ-HCH</td>
<td>0.01</td>
<td>0.00</td>
<td>0.03</td>
<td>0.01</td>
<td>0.20</td>
<td>50.0</td>
<td></td>
</tr>
<tr>
<td>HCHs</td>
<td>0.95</td>
<td>0.93</td>
<td>4.03</td>
<td>0.02</td>
<td>1.16</td>
<td>0.90</td>
<td>100.0</td>
</tr>
<tr>
<td>o,p′-DDE</td>
<td>2.82</td>
<td>N.D.</td>
<td>10.08</td>
<td>0.00</td>
<td>1.41</td>
<td>3.84</td>
<td>25.0</td>
</tr>
<tr>
<td>p,p′-DDE</td>
<td>6.20</td>
<td>N.D.</td>
<td>23.61</td>
<td>0.86</td>
<td>10.56</td>
<td>6.67</td>
<td>100.0</td>
</tr>
<tr>
<td>p,p′-DDD</td>
<td>0.18</td>
<td>N.D.</td>
<td>0.47</td>
<td>0.12</td>
<td>0.44</td>
<td>45.8</td>
<td></td>
</tr>
<tr>
<td>o,p′-DDT</td>
<td>0.10</td>
<td>0.11</td>
<td>0.44</td>
<td>N.D.</td>
<td>0.12</td>
<td>0.27</td>
<td>87.5</td>
</tr>
<tr>
<td>p,p′-DDT</td>
<td>0.21</td>
<td>0.08</td>
<td>0.74</td>
<td>N.D.</td>
<td>0.16</td>
<td>0.31</td>
<td>79.2</td>
</tr>
<tr>
<td>DDTs</td>
<td>8.28</td>
<td>16.26</td>
<td>26.16</td>
<td>0.94</td>
<td>13.51</td>
<td>8.86</td>
<td>100.0</td>
</tr>
<tr>
<td>HCB</td>
<td>1.00</td>
<td>2.10</td>
<td>3.02</td>
<td>0.35</td>
<td>1.67</td>
<td>1.35</td>
<td>100.0</td>
</tr>
<tr>
<td>Heptachlor</td>
<td>0.14</td>
<td>N.D.</td>
<td>0.45</td>
<td>N.D.</td>
<td>0.07</td>
<td>0.46</td>
<td>25.0</td>
</tr>
<tr>
<td>Isodrin</td>
<td>0.09</td>
<td>0.03</td>
<td>0.40</td>
<td>N.D.</td>
<td>0.05</td>
<td>0.37</td>
<td>79.2</td>
</tr>
<tr>
<td>α-Chlordane</td>
<td>0.02</td>
<td>N.D.</td>
<td>0.06</td>
<td>N.D.</td>
<td>0.01</td>
<td>0.49</td>
<td>33.3</td>
</tr>
<tr>
<td>γ-Chlordane</td>
<td>0.02</td>
<td>N.D.</td>
<td>0.05</td>
<td>N.D.</td>
<td>0.01</td>
<td>0.39</td>
<td>41.7</td>
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<tr>
<td>Chloradane</td>
<td>0.04</td>
<td>N.D.</td>
<td>0.11</td>
<td>N.D.</td>
<td>0.03</td>
<td>0.50</td>
<td>41.7</td>
</tr>
<tr>
<td>Endosulfan I</td>
<td>0.14</td>
<td>0.04</td>
<td>0.38</td>
<td>N.D.</td>
<td>0.12</td>
<td>0.30</td>
<td>83.3</td>
</tr>
<tr>
<td>Endosulfan II</td>
<td>0.08</td>
<td>0.01</td>
<td>0.25</td>
<td>N.D.</td>
<td>0.06</td>
<td>0.35</td>
<td>70.8</td>
</tr>
<tr>
<td>Endosulfan</td>
<td>0.21</td>
<td>0.06</td>
<td>0.63</td>
<td>N.D.</td>
<td>0.18</td>
<td>0.34</td>
<td>83.3</td>
</tr>
<tr>
<td>Methoxychlor</td>
<td>0.61</td>
<td>0.38</td>
<td>2.46</td>
<td>N.D.</td>
<td>0.59</td>
<td>0.61</td>
<td>91.7</td>
</tr>
<tr>
<td>OCPs</td>
<td>10.17</td>
<td>20.98</td>
<td>32.56</td>
<td>1.34</td>
<td>17.27</td>
<td>10.74</td>
<td>–</td>
</tr>
</tbody>
</table>

N.D.: not detected.

For C. erythrophorus, whose second dominant OCPs were HCHs (14.0%). DDTs were also found to be the dominant OCPs in the water and suspended solids from Lake Chaohu (Liu et al., 2012; He et al., 2014). The percentages of DDTs found in the aquatic biota (62.1–98.4%) were similar to those measured in suspended solids collected in the spring (68%) and summer (88%) (He et al., 2014).

Fig. 2(B) shows that, except in C. erythrophorus (23.6%) and P. hylacraniius (37.8%), β-HCH was the predominant HCH isomer in other species and ranged from 46.3% to 69.8%, followed by α-HCH, γ-HCH, and δ-HCH. α-HCH accounted for 46.3%, 55.8%, and 69.8% in C. carpio, P. hylacranius, and C. erythrophorus, respectively; whereas it represented less than 20% of OCP concentrations in the other species. The proportion of γ-HCH, similar to that of α-HCH, was 11.2% in C. chinensis and less than 5% in the other species. δ-HCH concentrations were very low, β-HCH levels in the water were similar to those found in fish, whereas γ-HCH concentrations were higher in the water and suspended solids than those in fish. Of the four HCH isomers, the high proportion of β-HCH in biota tissues might be attributed to its hydrophobic nature, stability, and lower rates of metabolism than other HCH isomers (Pandit et al., 2006; Sun et al., 2005; Hu et al., 2010); while, the low proportion of γ-HCH in biota tissues might be attributed to its higher vapor pressure, as well as its photochemical transformation and biodegradation to α-HCH in the environment (Strandberg et al., 1998). The high rates of α-HCH in C. carpio, P. hylacranius, and C. erythrophorus may have resulted in the high bioaccumulation factors (BAFs) and high biota-suspended solid accumulation factors (BSSFs) of α-HCH (please see Section 3.2.2 for details).

Fig. 2(C) illustrates the ratios of DDTs in the aquatic biota, water and suspended solids. p,p′-DDE was a dominant DDT component found in the aquatic biota, accounting for 55.0% (M. amblycephala) to 99.1% (L. modestus) of DDT levels, which is consistent with other studies in China (Guo et al., 2008; Zhou et al., 2008; Qiu and Zhu, 2010). However, the dominant DDT components in the water and suspended solids were α,p′-DDE and p,p′-DDT, respectively. A high ratio of α,p′-DDE (77.7%) to total DDTs in the water may be the result of inputs from gaseous α,p′-DDE (64.6%) though a
Fig. 2. The arithmetic mean percent composition of (A) OCPs, (B) HCHs and (C) DDTs in different species, water and suspended solids from Lake Chaohu (The concentrations of OCPs in water and suspended solids are taken from Liu et al. (2012) and He et al. (2014) with the authors’ permission).

water-gas exchange (Ouyang et al., 2013). Alternately, o, p’-DDE content may be overestimated because of the thermal degradation of o, p’-Cl-DDT during GC analysis (Qiu et al., 2005). The source of the high p, p’-DDE in the aquatic biota was clearly p, p’-DDT (and/or p, p’-Cl-DDT from dicofol) that entered Lake Chaohu with suspended solids through eroded soil or runoff, as well as through the atmospheric deposition of particulate matter. This means that suspended solids likely constitute the main source of p, p’-DDT to the lake, and thereby to the aquatic biota. The possible sources of DDTs such as o, p’-DDT and p, p’-DDT in the environment may stem
3.1.3. The influence of lipid content on OCP levels and composition in aquatic biota

Hydrophobicity and lipophilicity are chemical properties of OCPs; lipid content and composition can influence the residual OCP levels in biota (Kawai et al. 1988). The geometric mean lipid content (dry weight) in aquatic biota from Lake ChaoHu was 3.47% and ranged from 1.14% to 10.68%. The log-transformation reduced the kurtosis and skewness of the lipid data (Figure S2); therefore, the correlation between the log-transformed lipid and OCP content was studied (Table S3).

Table S3 illustrates significant correlations between the logarithms of lipid concentrations and the logarithms of contaminant concentrations, except for isodrin and methoxychlor. Linear relationships between lipid content and contaminants in aquatic biota were also found in multiple other studies (e.g., Nowell et al., 1999; Erdogru et al., 2005; Guo et al., 2008).

Figure S3 shows the differences in the lipid-normalized concentrations of OCPs by species. OCP levels in aquatic biota were ranked as follows: H. maculatus > C. chinensis > C. carpio > C. erythropterus > A. nobilis > M. amblycephala > L. modestus > P. hyalocranius. This order is different from that of the wet weight concentrations, reflecting the influence of lipids on contaminant concentrations.

3.2. The bioaccumulation of OCPs and the correlation with $K_{ow}$

3.2.1. The correlations between OCP levels in aquatic biota and the environment

Aquatic animals accumulate contaminants from two primary sources: water and suspended solids (Eqani et al., 2013; Arnot and Gobas, 2006; Campbell et al., 2000). The former enters aquatic biota via partitioning and the gills or skin; while the latter enters via dietary uptake (consumption of contaminated particles). A study focused on the correlations of contaminants in aquatic biota and environmental media (water and suspended solids), $p'$, $p''$-DDT was omitted from the correlation analysis because its concentration in the aquatic biota was extremely high, while its presence in the water and SS was extremely low; in addition, $p'$, $p''$-DDT in aquatic biota is typically a metabolite of $p'$, $p''$-DDT. $p'$, $p''$-DDT was also omitted for similar reasons. The concentrations of all other contaminants detected in all three media were log-transformed and analyzed using Pearson’s correlation test. The units of concentration in the biota, water, and suspended solids were ng/g lw, ng/l, and ng/L respectively. Fig. 3 indicates that the OCPs found in the aquatic biota correlate significantly with those found in the water and suspended solids at a 0.01 level ($r=0.694$, $p=0.003$, $N=16$) and 0.05 level of significance ($r=0.605$, $p=0.017$, $N=15$), respectively. The correlations between the OCP concentrations in each of the eight studied species and the environmental media were also analyzed. Table S4 shows that there were significant positive correlations between the OCP concentrations in C. erythropterus and those in both water and suspended solids, as well as between the OCP levels in P. hyalocranius and those in the suspended solids.

3.2.2. The bioaccumulation of OCPs in aquatic biota

The bioaccumulation factor is used to describe the process by which an organism absorbs contaminants from its environment and food (van der Oost et al., 2003). Bioconcentration is the accumulation of contaminants taken in by aquatic biota only through the gills or skin (Veith et al., 1979); a bioconcentration factor (BCF) is usually used to measure this accumulation and can only be measured under laboratory conditions. In field situations, a bioaccumulation factor (BAF) is usually employed. Another factor frequently used to evaluate contaminant accumulation is the BSSF (biota-suspended solid accumulation factor), which provides a measurement of contaminants in biota that feed on plankton (Hendriks et al., 1998; Burkhard and Lukasewycz, 2000). Together, the BAF and BSSF represent bioaccumulation from dissolved and suspended contaminants in the water.

![Fig. 3. Correlations between OCPs in aquatic biota and the environment (a, water; b, suspended solids).](image-url)
In this study, the BAF and BSSAF were calculated using the following equations:

\[
\text{BAF} = \frac{C_b}{C_w} \quad (3)
\]

\[
\text{BSSAF} = \frac{C_b}{C_s} \quad (4)
\]

where \(C_b\) is the mean lipid-normalized concentration of OCPs (ng/g lw) in aquatic biota, \(C_w\) is the mean concentration in water (ng/L), and \(C_s\) is the organic carbon standardized concentration in suspended solids (ng/g oc). The compound-specific LogBAF and BSSAF values for the studied aquatic biota are tabulated in Tables S5 and S6 in Appendix A, and the comparisons of the species-specific LogBAF and BSSAF values of DDTs, HCHs, HCB and total OCPs are presented in Fig. 4.

Fig. 4 and Tables S5 and S6 show that BAF and BSSAF values varied among aquatic biota. To analyze the significance between BAF and BSSAF values, an independent-samples t test was used. There were no significant differences \((p > 0.05)\) in the compound-specific BAF and BSSAF values for different species. However, significant differences \((p < 0.05)\) in the species-specific BAF and BSSAF values were found for total OCPs and for \(\alpha\)-HCH, \(\omega\)-DDE, and \(p, p'\)-DDT. There were very similar trends in species-specific BAF and BSSAF values for DDTs, HCB and total OCPs (Fig. 4). The greatest BAF and BSSAF values were found for DDTs \((p < 0.05)\) and were observed in the large carnivorous fish species \((H.\text{ maculatus} \text{ and } C.\text{ erythropterus})\), in the large omnivorous fish species \((C.\text{ carpio} \text{ and } A.\text{ nobilis})\), and in the bottom-dwelling omnivorous mollusk species \((C.\text{ chinensis})\); while the lowest values \((p < 0.05)\) were observed in the small-size carnivorous fish species \((P.\text{ hyalocranius})\) and small shrimp \((L.\text{ modestus})\). Mid-range values were observed in medium-sized herbivorous fish species \((M.\text{ ambylycepha})\). It has been suggested that bottom-dwelling omnivorous species that feed on suspended solids and/or sediments, such as molluscs \((C.\text{ chinensis})\) and mud carp \((C.\text{ carpio})\), may accumulate greater concentrations of contaminants \((Zhou\text{ et al., 1998}; Zhou \text{ and Wong, 2000}; Leung et al., 2010; Kwok et al., 2013)\) and that species that feed on algae and zooplankton, such as \(P.\text{ hyalocranius}\) and shrimp \((L.\text{ modestus})\), may accumulate contaminants to a lesser degree \((Zhou \text{ and Wong, 2000})\).

3.2.3. The relationship between \(K_{ow}\) and the bioaccumulation of OCPs

Significant correlations between the bioaccumulation factor and the octanol–water partition coefficient \((K_{ow})\) have been reported in many studies \((e.g., Fisk et al., 1998; Borgå et al., 2005;
3.3. The magnification factors of OCPs in the aquatic food web

3.3.1. The trophic levels of aquatic biota and food web magnification factors

Table S8 shows the trophic levels of the aquatic species investigated in this study. Pearson’s correlation test indicated that there were significant correlations between species trophic level and lipid-normalized concentrations of α-HCH and p,p′-DDD at the 0.01 significance level; whereas significant correlations for γ-chlordane and Endosulfan I were observed at the 0.05 level. This result illustrates the potential for biomagnification of OCPs up the food web in Lake Chaohu, a trend that is consistent with other studies (e.g., Hu et al., 2010; Skarphedinsdottir et al., 2010).

The food web magnification factor (FWMF) is an important measure of the enrichment of contaminants in the food chain and represents the increment of a contaminant’s lipid-normalized concentration in biota with an increase in trophic level. FWMF was determined by finding the linear regression slope of the natural logarithm-transformed contaminant concentration and trophic level (Fisk et al., 2001):

\[
\text{FWMF} = e^{b}
\]

where \(b\) is the slope. We calculated the FWMF of OCPs in aquatic organisms in Lake Chaohu to estimate the biomagnification of contaminants across species (shown in Table 2). The FWMF of OCPs ranged from 0.41 to 1.90, and five contaminant values were lower than 1, including α-HCH, γ-HCH, δ-HCH, p,p′-DDD, and p,p′-DDE. The FWMF value of γ-HCH was lower than that of α-HCH, which is consistent with studies such as that performed in Lake Baiyangdian (Hu et al., 2010). However, the FWMFs of DDTs and HCHs were lower than those reported in the Lake Baiyangdian study (Hu et al., 2010) and two marine food web studies (Hop et al., 2002; Skarphedinsdottir et al., 2010). These results suggest the biomagnification potential of OCPs in Lake Chaohu. However, the FWMF values of β-HCH, o,p′-DDE, and HCB were lower than 1, which differs from past studies (Skarphedinsdottir et al., 2010). These differences may be the result of the narrow food web in Lake Chaohu, which did not include birds or fish-eating mammals. It is assumed that the biomagnification of these three contaminants depends on the type of food web modeled (Hop et al., 2002), which requires further work.

### Table 2

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>(p) value</th>
<th>Slope</th>
<th>(R^2)</th>
<th>(K_{ow})</th>
<th>No. of species</th>
<th>FWMF</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-HCH</td>
<td>0.601</td>
<td>0.482</td>
<td>0.398</td>
<td>3.89</td>
<td>8</td>
<td>1.78</td>
</tr>
<tr>
<td>β-HCH</td>
<td>-0.254</td>
<td>-0.332</td>
<td>0.063</td>
<td>3.89</td>
<td>8</td>
<td>0.61</td>
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<tr>
<td>γ-HCH</td>
<td>0.299</td>
<td>0.213</td>
<td>0.095</td>
<td>3.89</td>
<td>8</td>
<td>1.12</td>
</tr>
<tr>
<td>δ-HCH</td>
<td>0.378</td>
<td>0.502</td>
<td>0.14</td>
<td>4.15</td>
<td>7</td>
<td>1.74</td>
</tr>
<tr>
<td>HCHs</td>
<td>0.050</td>
<td>0.056</td>
<td>0.0025</td>
<td>6</td>
<td>4</td>
<td>1.39</td>
</tr>
<tr>
<td>p,p′-DDE</td>
<td>0.276</td>
<td>0.193</td>
<td>0.596</td>
<td>6</td>
<td>2</td>
<td>0.72</td>
</tr>
<tr>
<td>p,p′-DDD</td>
<td>-0.216</td>
<td>-0.261</td>
<td>0.047</td>
<td>5.96</td>
<td>8</td>
<td>0.72</td>
</tr>
<tr>
<td>p,p′-DDE</td>
<td>-0.561</td>
<td>-0.675</td>
<td>0.291</td>
<td>6.20</td>
<td>5</td>
<td>0.75</td>
</tr>
<tr>
<td>p,p′-DDD</td>
<td>-0.607</td>
<td>-0.66</td>
<td>0.372</td>
<td>6.20</td>
<td>7</td>
<td>0.44</td>
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<tr>
<td>p,p′-DDD</td>
<td>0.505</td>
<td>0.058</td>
<td>0.0034</td>
<td>6.91</td>
<td>8</td>
<td>1.17</td>
</tr>
<tr>
<td>DDTs</td>
<td>0.430</td>
<td>0.425</td>
<td>0.1799</td>
<td>6.91</td>
<td>7</td>
<td>1.96</td>
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<tr>
<td>DDTs</td>
<td>-0.242</td>
<td>-0.296</td>
<td>0.0384</td>
<td>6.89</td>
<td>8</td>
<td>0.68</td>
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<tr>
<td>HCB</td>
<td>-0.381</td>
<td>-0.609</td>
<td>0.1357</td>
<td>8</td>
<td>0.41</td>
<td></td>
</tr>
<tr>
<td>Isodrin</td>
<td>-0.413</td>
<td>-0.653</td>
<td>0.1584</td>
<td>4.41</td>
<td>3</td>
<td>0.48</td>
</tr>
<tr>
<td>Heptachlor</td>
<td>-0.324</td>
<td>-0.341</td>
<td>0.1091</td>
<td>7</td>
<td>0.60</td>
<td></td>
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<tr>
<td>γ-Chlordane</td>
<td>-0.653</td>
<td>-0.579</td>
<td>0.4215</td>
<td>4</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>Endosulfan I</td>
<td>-0.531</td>
<td>-0.613</td>
<td>0.283</td>
<td>-1.70</td>
<td>7</td>
<td>0.59</td>
</tr>
<tr>
<td>OCPs</td>
<td>-0.204</td>
<td>-0.265</td>
<td>0.0409</td>
<td>8</td>
<td>0.69</td>
<td></td>
</tr>
</tbody>
</table>

Note: Log \(K_{ow}\) was the values in the references (Shen and Wania, 2005; Sabljic et al., 1995).

- Correlation is significant at the 0.05 level.
- Correlation is significant at the 0.01 level.

3.3.2. The relationship between FWMF and \(K_{ow}\)

Many studies have shown that the FWMF of OCPs is associated with the octanol–water partition coefficient (\(K_{ow}\)) of the marine food web. Contaminants become more hydrophobic and persistent and may become more likely to transfer through diet as \(K_{ow}\) increases (Nfon and Cousins, 2006; Skarphedinsdottir et al., 2010; Walters et al., 2011). We hypothesized that there was a similar trend in the freshwater food web. After the logarithm transformation, FWMF and log-\(K_{ow}\) were analyzed using Pearson’s test. No significant correlation was found (\(p>0.3\)), although a positive relationship was observed.

3.4. The human health risk assessment of OCPs in aquatic biota

The following assessment methods are widely used to evaluate human health risks: the acceptable daily intake (ADI) is utilized by the WHO, the minimal risk level (MRL) is used by the US FDA, and the potential carcinogenic risk is used by the US EPA (Li et al., 2008a). Each method has advantages and limitations. The ADI is simple to calculate; however, it is typically used to evaluate toxic effects without considering the duration of exposure. The MRL divides toxic effects into short-term, mid-term, and long-term; however, it does not recognize genetic variations or cancer risk. The EPA method identifies the human carcinogenic risk associated with contaminants. In this study, the EPA method was used to assess the health risk of OCPs in aquatic biota in Lake Chaohu.

The screening value is the maximum value of contaminants in edible tissues and organisms, as proposed by the US EPA. SVs were calculated as follows (U.S. EPA, 2000a):

\[
SV = \frac{RL \times BW}{SF \times CR}
\]

where SV is the maximum allowable level (μg/g); RL is the maximum acceptable risk (dimensionless); SF is the cancer slope factor (1/(mg/kg d)); BW is the average body weight (70 kg); and CR is the consumption rate (17.5 g/d for general adults and 142.2 g/d for subsistence fishers) (U.S. EPA, 2000a). Because the health risk assessment is focused on the intake of HCHs and DDTs from diet, the oral cancer slope factor, which is 0.35 for HCHs and 0.34 for DDTs, was used (U.S. EPA, 2000b). We set the acceptable risk level at \(10^{-5}\), which resulted in SVs of 14.06 ng/g ww and 14.48 ng/g ww for HCHs and DDTs found in the fish samples consumed by Zhou et al., 2008; Schackhamer et al., 1988); this correlation may be influenced by the growth rate, lipid content, habitat, and metabolism of aquatic biota (Wong et al., 2001; Liu and Xu, 2005). The bioaccumulation factor can be estimated using log \(K_{ow}\) values (Meylan et al., 1999), and different equations can be applied for different log \(K_{ow}\). For example, there is a positive correlation between the bioaccumulation factor and contaminants with log \(K_{ow}\) < 6, whereas there is negative correlations with contaminants that have a log \(K_{ow}\) > 6 (ICCA, 1998).

Therefore, we studied the relationship between the BAF or BSSAF of OCPs in aquatic biota and \(K_{ow}\) values. We used Spearman’s correlation test to analyze the relationship between the BAF or BSSAF and \(K_{ow}\) after the logarithm transformation was performed (Table S7). Significant positive correlations between BAF and BSSAF were observed for H. maculatus, C. chinensis and L. modestus; and significant correlations between BSSAF and \(K_{ow}\) were observed for C. chinensis and L. modestus. These findings are consistent with existing studies (Vives et al., 2005; Veltman et al., 2005) and could explain the observed lower BSSAF and BAF values for HCHs, which had lower \(K_{ow}\) values than HCBs and DDTs in this study (Russell et al., 1999; Ruus et al., 2002).

![Image of the document]
subsistence fishers, respectively; and 114.29 ng/g ww and 117.65 ng/g ww for general adults, respectively. The carcinogenic risks from HCHs and DDTs in the fish muscles are shown in Table 3.

The HCH concentrations ranged from 0.31 to 2.32 ng/g ww, which were lower than the screening values both for subsistence fishers and general adults, and therefore indicated low cancer risk. The DDT concentrations ranged from 1.20 to 23.67 ng/g ww, most of which were higher than the screening values for subsistence fishers, but lower than those for general adults. C. carpio, C. chiniensis, M. amblycephala, and A. nobilis, presented carcinogenic risks (Table 3).

4. Conclusions

In the present study, the criteria to determine the best bioindicators for monitoring OCP contamination in Lake Chaohu included the correlation between OCP concentrations in aquatic biota and concentrations in water and/or suspended solids. The best indicator for determining the human carcinogenic risk though consumption of aquatic organisms was mean wet weight OCP concentrations found in aquatic biota. Based on these criteria, C. erythropterus and P. hyalocrenus are the most sensitive bioindicators for monitoring OCP contamination in the water and suspended solids of Lake Chaohu because there were significant positive relationships between OCPs levels in Culter erythropterus and those in both water and suspended solids, as well as between OCPs levels in Protosalanx hyalocrenus and those in suspended solids. M. amblycephala had the highest mean wet weight OCP concentrations and serves as the most sensitive indicator for assessing the human carcinogenic risk.

DDTs were the predominant OCPs residuals found in aquatic biota in Lake Chaohu and resulted in potential risks to human health for those who consumed fish from Lake Chaohu. The mean bioaccumulation factor (BAF) and biota suspended solids accumulation factor (BSSAF) were highest for DDTs in this study. The food web magnification factors (FWMF) for p, p'-DDT were greater than 1, implying biomagnification. These findings indicate that DDTs still seriously threaten the ecosystems and human health in the study area and should be closely monitored because the agricultural application of DDT powder was officially banned in 1983.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ecolind.2015.06.026

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