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## **Environmental Impact Statement**

Few studies are available for understanding the seasonal distributions of PAHs and OCPs in water from the well-known hyper-eutrophic Lake Taihu. These hydrophobic contaminants could be easily further accumulated in phytoplankton, and then will either be grazed on and transported to other compartments of the pelagic food chain or carried to the sediment by live or dead cells and sinking aggregates. It is necessary to investigate the potential ecological effects of phytoplankton on the fate of hydrophobic organic compounds (HOCs), which will be helpful for elucidating the interactions between HOCs and eutrophication from a holistic approach.

The potential effects of phytoplankton on the occurrence of organochlorine
 pesticides (OCPs) and polycyclic aromatic hydrocarbons (PAHs) in water from
 Lake Taihu, China

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5 Abstract

6 Seasonal distribution of organochlorine pesticides (OCPs) and polycyclic aromatic 7 hydrocarbons (PAHs) and possible interactions with phytoplankton species in water from Lake Taihu, were investigated. OCP concentrations ranged from 69.95 to 223.08 8 ng  $L^{-1}$  in winter and from 80.95 to 376.03 ng  $L^{-1}$  in summer, while PAHs ranged from 9 45.40 to 232.74 ng  $L^{-1}$  in winter and 49.53 to 197.72 ng  $L^{-1}$  in summer. Such 10 11 physicochemical and biological parameters as the larger amounts of pollutants 12 uptaken by phytoplankton, and the increased atmospheric wet deposition, the discharge of wastewater, the resuspension of polluted sediments in summer time, were 13 14 responsible for the relative higher residues of both OCPs and PAHs than winter. 15 Canonical correspondence analysis (CCA) between phytoplankton biomass and micropollutants indicated high affinity of OCPs to *Bacillariophyta* and *Cryptophyta* 16 and PAHs to Cyanophyta and Chlorophyta, documenting the ecological effects of 17 18 phytoplankton on the biogeochemical processes of OCPs and PAHs and thus should be further investigated especially in hyper-eutrophic lakes. 19

# 20 Introduction

National and international pressure is mounting for water quality improvement in the twenty first century, and it is commonly known that a significant threat to water quality is posed by the discharge and dumping of wastes containing high levels of

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anthropogenic organic micropollutants such as polycyclic aromatic hydrocarbons 24 (PAHs) and organochlorine pesticides (OCPs).<sup>1</sup> PAHs and OCPs are typical toxic 25 organic pollutants and most are listed as priority pollutants by national organizations 26 due to their persistence, long-range transport, bioaccumulation and biological 27 toxicity.<sup>2,3</sup> They can enter the aquatic environment through different pathways. 28 including effluent discharge, agricultural runoff, atmospheric deposition, and air/water 29 exchange.<sup>4</sup> Therefore, PAHs and OCPs have been widely detected and become 30 31 ubiquitous pollutants in freshwater and marine aquatic ecosystems, and have received 32 considerable worldwide attention resulting from public awareness of environmental problems and expectations for a good quality of life.<sup>5,6</sup> 33

34 During the last decades, increased primary production has been observed in many 35 lakes and most coastal areas from enhanced anthropogenic inputs of nutrients. 36 Eutrophication in freshwater and coastal marine areas includes a series of processes that alter the ecosystems significantly.<sup>7</sup> An increased nutrient input causes a stepwise 37 change in productivity, with phytoplankton biomass increase being one of the most 38 39 obvious effects. Furthermore, increasing biomass and phytoplankton growth rates will finally influence the biogeochemical cycles of hydrophobic organic compounds 40 41 (HOCs), such as OCPs and PAHs, in aquatic environments due to the uptake of these pollutants by phytoplankton.<sup>8,9</sup> And then, contaminants accumulated in phytoplankton 42 will either be grazed on and transported to other compartments of the pelagic food 43 chain or carried to the sediment by live or dead cells and sinking aggregates.<sup>10</sup> It is 44 45 important to elucidate the effects of eutrophication on HOC uptake in phytoplankton, 46 and whether these effects are transferred to, and sustained through, the aquatic food webs. Few investigations have, however, addressed this issue. Traditionally, the 47 environmental effects of eutrophication and contaminants have been studied 48

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49 separately without a holistic approach.<sup>9</sup> In recent years, potential interactions of 50 eutrophication and contaminant cycling have been highlighted among other things, 51 resulted in the Eutrophication and CONtaminants (EUCON) research program of the 52 Swedish Environmental Protection Agency.<sup>11</sup> Although numerous investigations have 53 been conducted over the last decades on bioconcentration of HOCs by phytoplankton, 54 the influence of the biomass and community compositions of phytoplankton on the 55 fate of HOCs still remain to be clarified.<sup>12</sup>

The Yangtze River Delta is one of the most important economic engines of China, 56 characterized by fast urbanization and industrialization.<sup>13</sup> The Lake Taihu basin, the 57 58 heart of the Yangtze River Delta, is also an important grain production base in China 59 and as such has the highest pesticide application in the country. The basin covers only 60 0.4% of the total territory of the country but contributes 3.1% of the national food production and 10% of the gross domestic product. With rapid economic development 61 62 and population increases, man-made pollutants derived from household, agricultural, and industrial activities have been discharged into the water, resulting in serious 63 pollution of HOCs and eutrophication in Lake Taihu.<sup>14</sup> However, most previous 64 studies focused on the residual levels and possible ecological risk of PAHs and OCPs 65 in different environmental compartments including air, water, sediment, benthos, 66 fish.<sup>15-20</sup> Knowledge of the seasonal distribution of such pollutants in the water 67 column is lacking. Moreover, Lake Taihu has also experienced accelerated 68 69 eutrophication over the past 3 decades and has changed from a mesotrophic, 70 diatom-dominated lake to a hyper-eutrophic, Cyanophyta-dominated system, with *Microcystis* blooms now occurring regularly throughout much of the lake.<sup>21</sup> Since 71 72 most environmental decisions around this area are based on knowledge of separate effects of either HOCs or eutrophication, ignoring interactive processes that may 73

influence the overall effects, knowledge about potential interactive mechanisms is desirable both with respect to remedial action and as a basis for the development of environmental criteria and classification of contaminants with respect to risks.

The objective of the present study was to investigate the spatial and seasonal distribution of PAHs and OCPs in water samples from Lake Taihu, a hyper-eutrophic lake in China, and thus enhancing the public awareness of toxic organic pollutants in freshwater lakes. Moreover, we investigated the phytoplankton community structure and their possible effects on the fate of such hydrophobic chemicals to determine potential interactions between organic pollutants and eutrophication in lake ecosystem.

84 Materials and methods

## 85 Sampling

The detailed information of 15 sampling locations distributed over the whole lake are 86 shown in Fig. 1, included Meiliang Bay (TH1, TH2, TH3), Zhushan Bay (TH8), Lake 87 88 Center (TH4, TH9, TH10, TH12), Dapu Estuary (TH5), Jiapu Estuary (TH11), and 89 Xiaomei Estuary (TH6), South Lake Taihu (TH13, TH14, TH15) and East Lake Taihu 90 (TH7). Water samples for OCPs and PAH analysis were collected in January and 91 August 2010 corresponding to winter and summer samples, respectively. Surface 92 water samples at 0.5 cm depth were collected from each location using pre-cleaned 1L 93 brown glass bottles. The bottles were rinsed three times with samples and then carefully filled just to overflowing without passing air bubbles through the samples. 94 95 All water samples were filtered through GF/C fiber glass filters (2.0 µm pore size, 96 Whatman, Britain) in the laboratory to remove sand and debris, and then stored in the refrigerator at 4 °C prior to HOC extraction. The extraction of HOCs was completed 97

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Integrated water samples were taken using a 2 m long and 10 cm diameter plastic tube. Phytoplankton were then enumerated microscopically from samples fixed in Logul's iodine and sedimented for 48 h. Biovolumes (ind L<sup>-1</sup>) were calculated from cell numbers and cell size measurements. These biovolumes were converted to biomass based on the assumption that 1 mm<sup>3</sup> of volume equals 1 mg of fresh-weight biomass (mg L<sup>-1</sup>). Proportions of *Cyanophyta* (%) to total phytoplankton were calculated using biovolume values.

107 While for the chemical properties of the water samples, the suspended solids (SS, mg L<sup>-1</sup>) were obtained by filtering water samples (100-500 mL according to the 108 amount of particles) using GF/F (0.7 µm pore size, Whatman, Britain) fiberglass 109 110 filters which had been pre-combusted at 550 °C for four hours. The filters were 111 subsequently dried at 105 °C and weighed using an electrobalance with an accuracy 112 of 0.01 mg. The filtration (20 mL) was then used for the determination of dissolved organic carbon (DOC, mg  $L^{-1}$ ) by catalytic combustion technique, which was 113 114 completed by the Torch organic carbon analyzer (Torch, Teledyne Tekmar, USA, the 115 relative standard deviation (RSD) < 1.5%).

116 **Fig. 1**.

# 117 Chemicals

All chemicals and solvents used for OCP and PAH determination were pesticide grade and purchased from Supelco (USA). The purified water was obtained from a Milli-Q water system (Millipore, Bedford, MA, USA). OCP and PAH standards were also purchased from Supelco. PAH standard solution contains 16 priority PAHs, 122 including naphthalene (NaP), acenaphthylene (Any), acenaphthene (Ana), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), 123 124 benz[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), 125 benzo[k]flouranthene (BkF), benzo[a]pyrene (BaP), dibenz[ah]anthracene (DahA), 126 benzo[ghi]perylene (BghiP), and indeno[1,2,3-cd]pyrene (InP). OCP standard solution 127 contains  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ -HCH, heptachlor, heptachlor epoxide,  $\alpha$ - and  $\gamma$ -chlordane, aldrin, endrin, dieldrin, endosulfan I, endosulfan II, endrin aldehyde, endosulfan 128 129 sulfate, endrin ketone, p,p'-DDE, p,p'-DDD, p,p'-DDT, and methoxychlor. Both 130 stock standard solutions were dissolved in suggested solvents with 131 methanol/dichloromethane (1:1, v/v) for PAHs and n-hexane for OCPs, respectively. 132 The working solutions were stored at 4 °C and daily prepared as needed with suitable 133 dilutions before use.

# 134 HOC extraction

135 The filtered samples were extracted by solid phase extraction system equipped with 136 C18-boned phase columns (500 mg/6 mL of reversed phase octadecyl) purchased 137 from Supelco (USA). The column was conditioned with 20 mL methane followed by 20 mL deionized water at the rate of 5 mL min<sup>-1</sup>. The filtered water samples (1 L) 138 139 were then injected to the cartridge, and the absorbed compounds were eluted with 10 140 mL methane and 20 mL dichloromethane. The elutions were combined and dried 141 through sodium sulfate (baked at 400 °C for 5 h) and then were evaporated to nearly 1 142 mL using a rotary evaporator (BUCHI 250, Sweden). Next, n-hexane was added to 143 redissolve the extractions and transferred to a 5mL amber vial for further purification by a silica-alumina powder column (2:1) according to Zhao et al.<sup>24</sup> The target elutions 144 145 were collected and evaporated to near dryness with n-hexane as the substitute solvent 146 for the following instrumental analysis.

## 147 Quantitative determination of HOCs

The purified sample extracts for OCP analysis were quantitatively analyzed using an Agilent 7890 gas chromatograph equipped with a  $^{63}$ Ni µ-electron capture detector (GC-µECD) and a HP-5MS fused silica capillary column (30 m × 0.25 mm × 0.25 µm, J&W Scientific Inc., USA). PAHs were determined by high performance liquid chromatography (HPLC) equipped with a diode-array detector (DAD) and a series-wound fluorescene detector (FLD). Detailed instrumental conditions can be found in Zhao et al.<sup>25,26</sup>

155 Identification of PAHs and OCPs was based on the retention time of standard 156 components analyzed under the same instrument conditions, while the quantification 157 was completed by the external standard method. The method detection limits of 158 individual compounds using the present methods were determined as the 159 concentration of analytes in a sample that yield a peak signal-to-noise ratio (S/N) of 3. in the range of 0.01-3.52 ng  $L^{-1}$  for PAHs and 0.01-2.57 ng  $L^{-1}$  for OCPs, respectively. 160 161 For each set of samples, a procedure blank and a spiked sample consisting of all 162 reagents were run to check for interference and cross contamination. Results of 163 laboratory blanks indicated no interferent contaminants were detected during the tests, 164 and the spiked recoveries performed with deionized water ranged from 75% to 105% 165 for PAHs and from 78% to 112% for OCPs, respectively. Relative standard deviations 166 conducted with standard solutions were all less than 5% for both compounds. Additionally, standard solution was added every 15 samples to recalibrate the 167 168 retention time of target compounds.

#### 169 Statistical analysis

170 Statistical treatment of the obtained results and related correlation analysis were 171 performed with SPSS software (SPSS 16.0 for Windows, USA). Spearman's rank 172 correlation was used to test the strength of associations between parameters, and the statistical significance was considered for p < 0.05 (two-tailed tests). Canonical 173 174 correspondence analysis (CCA, CANOCO 4.5 for Windows, USA), a simple method for arranging biological species along environmental variables, was also used to 175 176 examine the features of the distributions of species along the environmental variables to determine the maximum correlations between pollutant concentrations and the 177 178 biomass of phytoplankton species.

# 179 **Results and discussion**

## 180 Concentrations and distribution of OCPs and PAHs

181 The concentrations and distribution of OCPs and PAHs in water samples collected in 182 winter and summer from Lake Taihu are shown in Fig. 2. In winter, the concentrations of OCPs ranged from 69.95 to 223.08 ng L<sup>-1</sup>. The highest concentration was found at 183 Meiliang Bay (TH1), followed by the Lake Center area (TH10: 207.56 ng L<sup>-1</sup>) and 184 Dapu Estuary (TH5: 185.70 ng L<sup>-1</sup>), while the lowest concentration was detected at 185 East Lake Taihu (TH7). Low OCP residues with 87.89 ng L<sup>-1</sup> concentration were also 186 187 observed at the Lake Center area (TH4). Compared to the higher concentrations of 188 OCPs detected in parts of the estuary regions (Dapu Estuary TH5 and Jiapu Estuary TH11: 160.17 ng  $L^{-1}$ ), OCPs were found at a lower concentration of 98.42 ng  $L^{-1}$  at 189 190 Xiaomei Estuary, which might be attributed to the different input burdens around this area.<sup>15</sup> In summer, OCPs were found ranging from 80.95 to 376.03 ng L<sup>-1</sup>, and the 191 192 highest and lowest concentrations were detected at the Jiapu Estuary (TH11) and

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193 South Lake Taihu (TH15), respectively. Higher residues were also found at Meiliang 194 Bay (TH1), Centre Lake (TH4), and Xiaomei Estuary (TH6) than other sampling sites, with the observed values of 321.89, 259.58 and 253.75 ng L<sup>-1</sup>, respectively. Compared 195 196 with the winter samples, higher values were found in summer except for sites TH5, 197 TH10, TH11, and TH12. Additionally, variance analysis performed by independent 198 samples T-test indicated significant variance was observed between the two seasons 199 based on the concentrations of total OCPs (p=0.039<0.05, n=15), thus demonstrating 200 the seasonal difference of OCPs in water column from Lake Taihu.

201 As for PAHs, they were found with concentrations ranging from 45.40 to 232.74 ng  $L^{-1}$  and the coefficient of variance among different sites was 0.57 in winter. The Jiapu 202 203 Estuary (TH11) had the highest residual level, followed by the Centre Lake area (TH10: 231.77 ng  $L^{-1}$ ) and South Lake Taihu (TH13: 225.92 ng  $L^{-1}$ ), while TH4 had 204 205 the lowest value. The Meiliang Bay, including sites TH1, TH2, and TH3, also had high concentrations of 137.56, 68.20, and 129.48 ng L<sup>-1</sup>, respectively, which may be 206 207 related to the extensive discharge of pollutants around these areas. Industries in the 208 area surrounding Meiliang Bay are primarily composed of machine shops, paper mills, 209 textile mill, chemical plant, leather industries power plants, and other manufactures, all of which contributed to the relative high PAH residues in Meiliang Bay.<sup>20</sup> PAHs in 210 211 the estuaries such as Dapu Estuary (TH5) and Xiaomei Estuary (TH6) were 69.76 and 131.02 ng L<sup>-1</sup>, respectively, possibly indicating a heavy discharge of wastewater from 212 213 tributaries, which was consistent with a significant positive relationship between drainage area and the level of PAHs suggested by Weinstein et al.<sup>27</sup> In summer, PAHs 214 ranged from 49.53 to 197.72 ng L<sup>-1</sup> with the highest concentration at Xiaomei Estuary 215 (TH6), followed by Meiliang Bay TH1 (197.39 ng  $L^{-1}$ ) and TH3 (193.43 ng  $L^{-1}$ ), and 216 the lowest concentration was observed at South Lake Taihu (TH13). A high PAH 217

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residue of 191.56 ng L<sup>-1</sup> was also found in Zhushan Bay, one of the most polluted areas in Lake Taihu due to the two severely polluted rivers (Taige Canal and Caoqiao River) carrying contaminants directly into the lake.<sup>16</sup> Similar seasonal distribution of higher residues of both OCPs and PAHs were observed in winter and summer for several sites (TH10, TH11, and TH12), while PAHs found at other sites were higher in summer than winter, although no significant difference was detected (p=0.738>0.05, n=15).

225 **Fig. 2**.

## 226 Seasonal variations of OCPs and PAHs

As for the seasonal differences, most samples showed higher residues of PAHs in 227 summer than in winter time except for several sites (TH10, TH11, TH12, TH13) as 228 229 suggested by the abovementioned analysis. OCPs were also found the similar seasonal 230 variation with 73.3% of samples had higher concentrations than in summer. 231 Atmospheric deposition is considered to be an important input of PAHs to surface 232 waters; 10-80% of PAH inputs to the world's oceans are estimated to originate from atmospheric sources.<sup>28</sup> Total PAH atmospheric inputs to the Mediterranean Sea are 233 estimated to be 3570 t yr<sup>-1</sup>, with a mean value of 47.5 t yr<sup>-1</sup>, whereas the total PAH 234 riverine inputs are about 5.3 and 1.3 t yr<sup>-1</sup> from the Phone and Ebro rivers, 235 respectively.<sup>29</sup> Among atmospheric deposition, inputs of such pollutants to lakes due 236 237 to rainwater on numerous occasions have been shown to contain many organic compounds including PAHs, and the concentration of PAHs in rainfall can sometimes 238 be much higher than in the receiving waterbody.<sup>30</sup> The dry and wet particle deposition 239 of dichlorodiphenyltrichloroethanes (DDTs) was more important than deposition 240 through the air-water exchange in the Great Lakes;<sup>15</sup> therefore, seasonal variations of 241

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242 micropollutants were consistent with the seasonal distributions of rainfall with higher243 rates in summer but lower rates in winter.

244 Furthermore, seasonal variation of PAHs and OCPs could be attributed to the 245 increased discharge of wastewater through tributaries during summer. The Taihu 246 Region is highly industrialized and surrounded by many industrial factories, 247 agricultural fields, livestock and aquaculture farming, and high-density populations, which may discharge more contaminants directly into the lake,<sup>20</sup> especially in summer 248 249 due to the increased water flow from surrounding tributaries. In addition, as a typical 250 large shallow lake, resuspension of sediments induced by the heavier wind-wave disturbance would also change the residues of pollutants in the aquatic phase.<sup>31</sup> SS in 251 252 water were higher in winter samples than in summer samples (Table 1), especially for 253 the sites at Centre Lake (TH4, and TH10), the estuary areas (TH5, TH6, TH11), and 254 the southern areas (TH13, TH14, and TH15) dominated by grass. The higher winter values were attributed to the stronger wind velocity in winter.<sup>32</sup> We only noted higher 255 256 residues of PAHs winter than in summer at sites TH10, TH11, TH12, and TH13, and 257 higher winter OCPs at sites TH10, TH11, and TH12. This finding was consistent with 258 the seasonal variations of SS, thus demonstrating the limited influence of 259 micropollutant inputs to the water column by sediment resuspension compared to 260 atmospheric deposition and external discharge.

In addition, phytoplankton uptake coupled with air-water diffusive exchange will also have an effect on input of HOCs to the aquatic system, which thus finally determines their concentrations in water.<sup>10,33</sup> The transport of HOCs, apart from catchment area input, across the surface microlayer is driven by atmospheric deposition and counteracted by water-to-air volatilization.<sup>15</sup> This has also been demonstrated by Qiu et al.<sup>15</sup> that atmospheric transport and deposition of endosulfan I

was a source of this compound to Lake Taihu. Furthermore, the link between 267 268 phytoplankton bioaccumulation and air-water exchange has been demonstrated by a number of observations.<sup>34,35</sup> Dachs et al.<sup>36</sup> provided a first theoretical assessment of 269 270 the possible control of plankton biomass dynamics on both the water-dissolved phase and air-water exchange of hydrophobic chemicals. Polychlorinated biphenyls (PCBs) 271 272 and PAH concentration profiles observed in the water column, either in the dissolved 273 phase or absorbed to phytoplankton, were similar to those found in the gas phase, 274 which suggested that air-water exchange supported and might even control the PCB concentrations in phytoplankton.<sup>37</sup> As HOCs in the dissolved state were accumulated 275 276 by phytoplankton and later sedimented in association with sinking particles 277 accompanied by the crash of the plankton bloom, leading to a depletion of 278 dissolved-phase HOC concentration in surface water, promoting net diffusive transfer from the atmosphere to the surface water.<sup>33,38</sup> As a result, gaseous transport of 279 280 semivolatile HOCs was higher in eutrophic systems such as Lake Taihu especially in 281 summer due to the higher amount of phytoplankton (Table 1).

282 **Table 1**.

## 283 Species-specific affinity of phytoplankton to HOCs

A complex succession of different planktonic species will have different ecological implications of the fate of HOCs.<sup>12</sup> CCA is a nonlinear multivariate direct gradient analytical method, which combines correspondence analysis with multiple regressions and can provide detailed analysis of the relationships between biological species and the environment.<sup>39</sup> Researchers have recently begun to use CCA to examine the relationships between phytoplankton and water nutrient contents.<sup>40</sup> However, few studies have used this method to examine the ecological contributions of

phytoplankton to bioaccumulation of toxic organic pollutants.<sup>41</sup> CCA was then used 291 292 here to determine the potential effects of phytoplankton species on the fate of 293 micropollutants in the water column of Lake Taihu. First, detrended correspondence 294 analysis (DCA) of concentrations of both PAHs and OCPs demonstrated that the first 295 axis length of the gradient was <2.0, and then the correlation analysis between the 296 concentrations of micropollutants and phytoplankton biomass was completed by the 297 redundancy analysis (RDA). The 2, 3, 4, and 5 ring PAH congeners were all 298 distributed at the second quadrant (Fig. 3), showing positive correlations with 299 Aphanizomenon, Schroederia, and Ankistrodesmus and relative weak positive 300 correlations with Microcystis and Scenedesmus, which demonstrated that Cyanophyta 301 and *Chlorophyta* were the major phytoplankton species affecting PAH distributions in 302 the water column. For OCPs, the major components including chlordanes, aldrins, and 303 DDTs were distributed at the first quadrant, in accordance with the fate of Aulacoseira 304 and Asterionella, and HCHs were positively correlated with Cryptomonas. Therefore, 305 OCPs in water were mainly correlated with *Bacillariophyta* and *Cryptophyta*, while 306 PAH residues in water showed positive correlations with Cyanophyta and 307 Chlorophyta.

**Fig. 3**.

These relationships indicated the potential influence of phytoplankton on the biogeochemical cycling of micropollutants in aquatic ecosystems attributed to the species-specific accumulation of HOCs by different phytoplankton.<sup>10,12,42</sup> Phytoplankton uptake is a two-compartment process, with fast adsorption to the phytoplankton cell surface followed by diffusion into the matrix in a partitioning-like mechanism; therefore, the initial adsorption in the uptake of HOCs in phytoplankton can be affected by the chemical composition of the cell wall.<sup>42,43</sup> The muramine acid

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316 of Cyanophyta causes a lower uptake of HOCs than the phospholipid cell wall of eucarvotic phytoplankton, such as *Bacillariophyta*.<sup>10</sup> Additionally, the lipid quality 317 318 will also influence HOC uptake in phytoplankton. PCBs are generally deposited in the lipid stores of organisms, and Berglund et al.<sup>12</sup> found that lipid contents explained 319 320 most of the variation of PCB concentration in phytoplankton in 19 southern Swedish lakes.<sup>44</sup> The present study performed in Lake Taihu implied a higher accordance of 321 322 PAHs with Cyanophyta and Chlorophyta and OCPs with Bacillariophyta and 323 *Cryptophyta* due to the species-specific uptake process, and then the internal uptake 324 mechanisms should be elucidated in the future study for evaluating the effects of 325 phytoplankton community on the fate of HOCs in aquatic ecosystem.

## 326 Conclusion

327 Both OCPs and PAHs are ubiquitous pollutants distributed in waters of Lake Taihu. 328 The residual levels of OCPs were similar to those reported in previous studies, while 329 PAHs were one to two orders of magnitude lower. The concentrations of OCPs and 330 PAHs in the summer water column were slightly higher than in winter due to such 331 physicochemical and biological parameters as the atmospheric deposition, uptake by 332 phytoplankton, discharge of wastewater, and resuspension of polluted sediments. The 333 primary study on the interactions between eutrophication and HOCs based on CCA 334 analysis demonstrated species-specific accumulation of hydrophobic contaminants by 335 phytoplankton, which would play a vital role in determining the biogeochemical 336 cycling of HOCs in eutrophic lakes. Furthermore, potential interactive processes 337 between HOCs and eutrophication should be included from a holistic approach for 338 water quality improvement in the future.

#### 339 Acknowledgments

- We appreciate the financial support by the National Science Foundation of China (41201535, 41373017), the Natural Science Foundation of Jiangsu Province, China (BK2012503), the National Key Basic Research and Development Program (973 Program: 2012CB417005), and the National Basic Research Program of China (2012FY111800-03).
- 345 **References**
- 346 1 J. L. Zhou, H. Hong, Z. Zhang, K. Maskaoui, W. Chen, *Water Res.*, 2000, 34,
  347 2132-2150.
- 2 Z. Cao, Y. Wang, Y. Ma, Z. Xu, G. Shi, Y. Zhuang, T. Zhu, *J. Hazard. Mater.*, 2005,
  122, 51-59.
- 350 3 Z. Tang, Q. Huang, Y. Yang, X. Zhu, H. Fu, Ecotox. Environ. Safe., 2013, 87, 89-97.
- 351 4 R. W. Macdonald, T. Harner, J. Fyfe, *Sci. Total Environ.*, 2005, **342**, 75-86.
- 352 5 K.F. Chang, G.C. Fang, J.C. Chen, Y. S., Wu, Environ. Pollut., 2006, 142: 388-396.
- 353 6 U. Ali, J. H. Syed, R. N. Malik, A. Katsoyiannis, J. Li, G. Zhang, K. C. Jones, Sci.
- 354 *Total Environ.*, 2014, **476-477**: 705-717.
- 355 7 J. A. Camargo, A. Alonso. *Environ. Int.*, 2006, **32**: 831-849.
- 356 8 J. S. Gunnarsson, D. Broman, P. Jonsson, M. Olsson, R. Rosenberg, *Ambio.*, 1995,
  357 24, 383-385.
- 358 9 J. Skei, P. Larsson, R. Rosenberg, P. Jonsson, M. Olsson, D. Broman, *Ambio.*, 2000,
- **29**, 184-194.
- 360 10 O. Berglund, P. Larsson, G. Ewald, L. Okla, *Ecology*, 2001, **82**, 1078-1088.
- 361 11 M. Meili, P. Jonsson, R. Carman, *Ambio.*, 2000, **29**, 282-287.
- 362 12 A. Gerofke, P. Komp, M. S. Mclachlan, Environ. Toxicol. Chem., 2005, 24,
- 363 2908-2917.

364	13 Z. Tang, Q. Huar	g, Y. Yang, Z	X. Zhu, H.	Fu, Ecotox.	Environ. Safe.	, 2013, <b>87</b>
365	89-97.					

- 366 14 G. Liu, G. Zhang, Z. Jin, J. Li, *Environ. Pollut.*, 2009, 157, 2994-3000.
- 367 15 X. Qiu, T. Zhu, F. Wang, J. Hu, Environ. Sci. Technol., 2008, 42, 1928-1932.
- 368 16 X. Wang, J. Xu, C. Guo, Y. Zhang, Bull. Environ. Contam. Toxicol., 2012, 89,
  369 1235-1239.
- 370 17 D. Wang, Y. Yu, X. Zhang, S. Zhang, Y. Pang, X. Zhang, Z. Yu, M. Wu, J. Fu,
  371 *Ecotox. Environ. Safe.*, 2012, **82**, 63-70.
- 372 18 H. Wang, C. Wang, W. Wu, Z. Mo, Z. Wang, Chemosphere, 2003, 50, 557-562.
- 373 19 Y. Zhang, Y. Lu, J. Xu, T. Yu, W. Zhao, *Bull. Environ. Contam. Toxicol.*, 2011, 87,
  374 80-85.
- 375 20 G. Guo, F. Wu, H. He, R. Zhang, C. Feng, H. Li, M. Chang, *Environ. Monit.*376 Assess., 2012, 184, 6815-6825.
- 377 21 H. W. Paerl, H. Xu, M. J. McCarthy, G. Zhu, B. Qin, Y. Li, W. S. Gardner, *Water*378 *Res.*, 2011, 45, 1973-1983.
- 379 22 Y. Chen, B. Qin, K. Teubner, M.T. Dokulil, J. Plankton Res., 2003, 25, 445-453.
- 380 23 Y. Chen, C. Fan, K. Teubner, M. Dokulil, *Hydrobiologia*, 2003, **506-509**: 273-279.
- 381 24 Z. Zhao, L. Zhang, J. Wu, C. Fan, *Chemosphere*, 2009, 77, 1191-1198.
- 25 Z. Zhao, Y. Wang, L. Zhang, Y. Cai, Y. Chen, *Environ. Sci. Pollut. Res.*, 2014, 21,
  8740-8749.
- 384 26 Z. Zhao, L. Zhang, Y. Cai, Y. Chen, *Ecotox. Environ. Safe.*, 2014, **104**, 323-331.
- 27 J. E. Weinstein, K. D. Crawford, T. R. Garner, *Environ. Monit. Assess.*, 2010, 162,
  21-35.
- 387 28 J. W. Moore, S. Ramamoorthy, in Organic Chemicals in Natural Waters: Applied
- 388 Monitoring and Impact Assessment, ed. R. S. Desanto, Springer-Verlag, New York,

389 **1984**.

- 390 29 E. Lipiatou, J. Tolosa, R. Simó, J. Bouloubassi, J. Dachs, S. Marti, M. A. Sicre, J.
- 391 M. Bayona, J. O. Grimalt, A. Saliott, J. Albaiges, Top. Stud. Oceanogr., 1997, 44,
- **392 881-905**.
- 393 30 E. Manoli, C. Samara, *Trend. Anal. Chem.*, 1999, 18, 417-428.
- 394 31 K. Shi, Y. Zhang, G. Zhu, X. Liu, Y. Zhou, H. Xu, B. Qin, G. Liu, Y. Li, Remote
- *Sens. Environ.*, 2015, **164**: 43-56.
- 396 32 Y. Zhang, B. Qin, W. Chen, L. Luo, Resources and Environment in the Yangtze
- 397 Basin, 2004, **13**, 266-271. (in Chinese)
- 33 S. N. Meijer, J. O. Grimalt, P. Fernandez, J. Dachs, *Environ. Pollut.*, 2009, 157,
  1815-1822.
- 400 34 P. Larsson, L. Okla, G. Cronberg, Can. J. Fish. Aquat. Sci., 1998, 55: 1926-1937.
- 401 35 R. Bruhn, M. S. McLachlan. Mar. Pollut. Bull., 2002, 44: 156-163.
- 402 36 J. Dachs, S. J. Eisenreich, J. E. Baker, F. C. Ko, J. D. Jeremiason, Environ. Sci.
- 403 *Technol.*, 1999, **33**: 3653-3660.
- 404 37 J. Dachs, S. J. Eisenreich, R. M. Hoff, *Environ. Sci. Technol.*, 2000, **34**, 1095-1102.
- 405 38 L. Nizzetto, R. Gioia, J. Li, K. Borgå, F. Pomati, R. Bettinetti, J. Dachs, K. C.
- 406 Jones, *Environ. Sci. Technol.*, 2012, **46**: 3204-3211.
- 407 39 C. J. F. ter Braak, P. F. M. Verdonschot, Aquat. Sci., 1995, 57, 255-289.
- 408 40 X. Liu, X. Lu, Y. Chen, *Harmful Algae*, 2011, **10**, 337-343.
- 409 41 Z. Zhao, Y. Jiang, L. Xia, T. Mi, W. Yan, Y. Gao, X. Jiang, E. Fawundu, J. Hussain,
- 410 Environ. Sci. Pollut. Res., 2014, 21, 3091-3103.
- 411 42 M. Seto, I. C. Handoh. Chemosphere, 2009, 77: 679-686.
- 412 43 J. Dachs, R. Lohmann, W. A. Ockenden, L. Mejanelle, S. J. Eisenreich, K. C. Jones,
- 413 Environ. Sci. Technol., 2002, **36**, 4229-4237.

- 414 44 S. D. Vento, J. Dachs, *Environ. Toxicol. Chem.*, 2002, **21**, 2099-2107.
- 415 45 S. G. Lynn, D. J. Price, W. J. Birge, S. S. Kilham, Aqua. Toxicol., 2007, 83, 24-32.

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## 417 Figure captions

- 418 Fig. 1 Sampling locations in Lake Taihu (fifteen samples distributed over the whole
- 419 lake from TH1 to TH15 included).
- 420 Fig. 2 Seasonal concentrations of OCPs (a) and PAHs (b) detected in surface waters
- 421 of Lake Taihu.
- 422 Fig. 3 RDA ordination biplots of PAH and OCP residues and predominant
- 423 phytoplankton communities in the Lake Taihu water column. (Mic: Microcystis; Sce:
- 424 Scenedesmus; Ank: Ankistrodesmus; Sch: Schroederia; Aph: Aphanizomenon; Aul:
- 425 Aulacoseira; Ast: Asterionella; Cry: Cryptomonas).

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427 Table 1 Winter and summer physicochemical and biological characters of water

428 samples from Lake Taihu. (Site designations refer to sampling station locations in Fig.

429 1)

	Winter					Summer				
	SS	DOC	Cyanophyta	Phytoplankton		SS	DOC	Cyanophyta	Phytoplankton	
Sites	mg L <sup>-1</sup>	mg L <sup>-1</sup>	%	ind L <sup>-1</sup>	mg L <sup>-1</sup>	mg L <sup>-1</sup>	mg L <sup>-1</sup>	%	ind L <sup>-1</sup>	mg L <sup>-1</sup>
TH1	28.8	7.12	71.7	3.E+07	13.04	25.9	2.26	98.2	28.8	7.12
TH2	41.5	6.29	60.9	2.E+07	18.50	29.0	2.50	98.0	41.5	6.29
TH3	34.4	7.47	75.7	1.E+07	6.45	30.7	2.36	98.2	34.4	7.47
TH4	123.5	6.86	90.9	9.E+06	3.34	28.2	1.92	99.5	123.5	6.86
TH5	117.1	8.62	90.7	3.E+06	1.16	44.7	2.11	96.8	117.1	8.62
TH6	109.0	4.02	72.7	2.E+06	2.52	63.8	0.96	90.9	109.0	4.02
TH7	58.6	4.53	48.6	5.E+06	9.03	9.3	1.77	32.3	58.6	4.53
TH8	65.3	4.15	71.3	6.E+06	4.33	27.6	3.58	98.7	65.3	4.15
TH9	75.8	4.50	96.9	1.E+07	1.60	37.3	2.74	99.8	75.8	4.50
TH10	117.0	4.77	98.6	5.E+06	0.44	26.3	1.56	91.2	117.0	4.77
TH11	125.8	5.66	82.4	2.E+06	1.69	29.7	2.65	83.2	125.8	5.66
TH12	113.4	4.89	99.5	1.E+07	0.57	56.1	2.72	98.6	113.4	4.89
TH13	142.9	5.27	99.5	1.E+07	0.81	66.6	1.30	100.0	142.9	5.27
TH14	115.1	4.74	87.9	4.E+06	1.42	28.0	1.99	97.6	115.1	4.74
TH15	124.6	5.33	97.0	2.E+06	0.18	4.0	2.09	90.9	124.6	5.33

430



Fig. 1 Sampling locations in Lake Taihu (fifteen samples distributed over the whole lake from TH1 to TH15 included).



Fig. 2 Seasonal concentrations of OCPs (a) and PAHs (b) detected in surface waters of Lake Taihu.



Fig. 3 RDA ordination biplots of PAH and OCP residues and predominant phytoplankton communities in the Lake Taihu water column. (*Mic: Microcystis; Sce: Scenedesmus; Ank: Ankistrodesmus; Sch: Schroederia; Aph: Aphanizomenon; Aul: Aulacoseira; Ast: Asterionella; Cry: Cryptomonas*).