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Assessment of Sediment Risk in the North End of Tai Lake, China: Integrating Chemical Analysis and Chronic Toxicity Testing with *Chironomus dilutus*

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Abstract Whole life-cycle bioassays with *Chironomus dilutus* were performed to evaluate sediment toxicity in Tai Lake, a typical freshwater lake in China. Meanwhile, contaminants of concern were analyzed in sediment. The sediments in Tai Lake showed no acute mortality in 10-day testing to *C. dilutus*. After chronic exposure to the sediments, however, adverse effects—including decreased survival and sublethal impairments of growth, emergence, and fecundity—were observed at most sites in Tai Lake. A variety of contaminants were detected in sediment with the total concentrations in the range of 504–889 ng/g dry weight (dw) for polycyclic aromatic hydrocarbons, 0.56–1.81 ng/g dw for polychlorinated biphenyls, 38.6–87.8 ng/g dw for polybrominated diphenyl ethers, 8.34–14.2 ng/g dw for organochlorine pesticides, 1.27–2.95 ng/g dw for organophosphate pesticides, 0.11–0.21 ng/g dw for pyrethroid pesticides, and 332–609 µg/g dw for metals. Finally, a canonical correlation analysis was applied to link chronic sediment toxicity to the toxic units of individual contaminants. Results suggested that two pesticides (hexachlorocyclohexane and chlorpyrifos) and two metals (chromium and nickel) in sediments from Tai Lake were the potential contributors to the noted toxicity in *C. dilutus* in the life-cycle toxicity testing. In conclusion, acute bioassays with the benthos were not sensitive enough to assess sediment toxicity in freshwater lakes in China, and it is desirable to integrate chronic toxicity testing with chemical analysis to better understand sediment risk.

Water quality in freshwater lakes in China has experienced severe deterioration in recent decades. In addition to eutrophication (Duan et al. 2009), high concentrations of organic contaminants (Wang et al. 2012a) and metals (Ma et al. 2013) in the lakes are of great concern. Tai Lake is a shallow freshwater lake with a mean depth of 1.9 m and an area of 2428 km^2; it ranks as the third largest freshwater lake in China; and it is situated on the southern part of the Yangtze River Delta. This lake provides drinking-water resources to surrounding cities and receives waters from nearby urban and agricultural areas. With economic development and urbanization in its watershed, increased concentrations of legacy contaminants, such as polycyclic aromatic hydrocarbons (PAHs) (Lei et al. 2014), organochlorine pesticides (OCPs) (Wang et al. 2012a), and metals (Fu et al. 2013), were frequently found in the lake. Furthermore, emerging contaminants, e.g., organophosphate (OPs) and pyrethroid pesticides (PYRs), were also detected in lake sediment (Wang et al. 2012b).

Sediment serves as a sink and a source for hydrophobic contaminants, and water quality is directly related to sediment quality (Förstner 2004). Integrating chemical analysis and toxicity testing with benthic organisms has been proposed to assess sediment quality (USEPA 2000). Although the lake sediments in China have been analyzed for various contaminants of concern (Wang et al. 2012a; Fu et al. 2013; Lei et al. 2014), the link between contaminants with sediment toxicity to benthic organisms is still unclear. Previous

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studies performed in urban waterways in South China reported extremely high mortality of *Chironomus dilutus* after 10-day sediment exposures (Mehler et al. 2011; Li et al. 2013; Sun et al. 2015). Nevertheless, our preliminary study showed that none of the sediment samples collected from freshwater lakes in China caused acute mortality to *C. dilutus*. Therefore, a hypothesis was made that the acute toxicity testing was not suitable for sediments in freshwater lakes. It is desirable to apply more sensitive bioassays to evaluate sediment toxicity in this situation, for instance, for assessing sublethal effects of benthic organisms after whole life-cycle toxicity testing (Benoit et al. 1997).

The objectives of the present study were to evaluate the chronic effects on survival, growth, emergence, and reproduction of *C. dilutus* after exposing them to the sediments from Tai Lake to analyze contaminants of concern in sediment, to integrate toxicity testing with chemical analysis using a screening toxic unit (TU) approach, and finally to identify potential contaminants that were responsible for the chronic toxicity in midges.

Materials and Methods

Sediment Collection and Acute-Toxicity Testing

As shown in Fig. S1 and Table S1 in the Supplementary Material ("s" represents figures and tables in the Supplementary Material thereafter), five sediment samples were collected from the north end of Tai Lake where water quality is significantly degraded (Wang et al. 2011; Lu et al. 2013). Among them, two were sampled from Meiliang Bay (T1 and T2), and the remaining three samples were from Zhushan Bay (T3), Gong Bay (T4), and the outlet to Wangyu River (T5), which is adjacent to Yangtze River and serves as a conveying water district. Meanwhile, a control sediment was collected from a drinking-water reservoir in Conghua, China. This sediment exhibited no chronic toxicity to the midges and contained no target contaminants at concentrations greater than the reporting limits (RLs) (Du et al. 2013, 2014).

Surface sediments were sampled using a stainless steel grab, immediately transported back to the laboratory, passed through a 0.5-mm sieve, and homogenized. The sediments used for toxicity testing and chemical analysis were stored at 4 and −20 °C, respectively. Acute toxicity was tested using *C. dilutus* for the sediments, and the test method is presented in the Supplementary Material.

Chronic-Toxicity Tests

Life-cycle toxicity tests using *C. dilutus* were performed in triplicate for each group according to a previously published method (Du et al. 2013). In brief, the test was initiated from newly hatched midge larvae (<24 h old) and terminated on the hatch of the second generation. Twenty midges were randomly distributed into a beaker that contained 60 g of wet sediment and 250 mL of overlying reconstituted water. Considering their physiological difference at different life stages, midge larvae were fed once daily with 1 mL of fish food at varying concentrations as follows: no food on day 1; 0.6 g/L on days 2 through 7; 3 g/L on days 8 through 12; and 6 g/L on day 13 to the end of the testing.

Lethality was enumerated at day 20 (before pupation) by sieving the midges from the sediment. Sublethal endpoints included the impairments of growth, emergence, and reproduction. Decrease in growth was quantified by comparing ash-free dry weight (AFDW) of the midges in site sediments with that in the control. After 20-day exposure, surviving *C. dilutus* were sieved from the sediment, cleaned, and dried at 60 °C for 3 days to obtain a constant weight (W1); then the organisms were reweighed after burning at 550 °C for 3 h (W2), and AFDW was the difference between W1 and W2.

To evaluate the impairment of emergence, cumulative emergence and emergence time were calculated by recording the number of midges that emerged daily from the time of the first emergence to the termination of the tests (47 days). Once the midges emerged, the adults were transferred from exposure beakers to collection chambers, and adverse effects of sediment exposure on the reproduction were assessed by the number of eggs per female; eggs were then counted under a microscope by the ring count method suggested by Benoit et al. (1997). In addition, egg hatchability was counted after a 7-day hatching period.

Chemical Analysis

Sediment samples were analyzed for a variety of chemical of concern including six classes of organic contaminants [16 PAHs, 27 polychlorinated biphenyls (PCBs), 8 polybrominated diphenyl ethers (PBDEs), 20 OCPs, 8 OPs, and 8 PYRs] (Table S2) as well as 7 metals [arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn)]. The details on chemicals and reagents and the procedures for chemical analysis and quality assurance and quality control are shown in the Supplementary Material. The contents of total organic carbon (OC) in sediment samples were quantified using an elemental analyzer (Elementar Vario EL III; Hanau, Germany) after removing inorganic carbon with 1 mol/L HCl.

Data Analysis

To assess the contribution of contaminants to sediment toxicity, TUs of individual compounds were calculated. As shown in Eq. (1), TU is the ratio of OC-normalized sediment concentration of a contaminant ($C_{\mathrm{s,oc}}$) and its chronic median effective concentration (EC_{50}). The sum of TUs of a group of contaminants was used to describe mixture toxicity assuming that the joint toxicity was concentration addition (Belden et al. 2007).

$$\mathrm{TU} = \frac{C_{\mathrm{s,OC}}}{\mathrm{EC}_{50}} \tag{1}$$

Statistical comparisons of sediment toxicity between the control and test sediments were performed by a one-way analysis of variance (ANOVA),and significant differences ($p < 0.05$) indicated that test sediments were toxic to the midges.

The relationships between the observed chronic toxicity and the TUs of contaminants were evaluated by a canonical correlation analysis (Liu et al. 2009). This procedure described the linear relationship between two sets of variables, which were denoted as X_1, X_2, …, X_m and Y_1, Y_2, …, Y_n. The respective coefficients (a_{i1}, a_{i2}, … a_{im} and b_{i1}, b_{i2}, … b_{in}) were modeled to achieve the correlation between the variables U_i and V_i (Eqs. 2, 3).

$$U_i = a_{i1}X_1 + a_{i2}X_2 + \cdots + a_{im}X_m \tag{2}$$

$$V_i = b_{i1}Y_1 + b_{i2}Y_2 + \cdots + b_{in}Y_n \tag{3}$$

The highest correlation between the pair of variables U_i and V_i was named as the first pair of canonical correlation—Corr (U_1, V_1)—and ρ_1 is their correlation coefficient. The second pair of maximally correlated variables was selected in turn, and tests of significance for canonical correlation coefficients were performed using a likelihood ratio test ($p < 0.05$). In the current study, adverse effects of survival, emergence, growth, fecundity, and hatchability were set as the X variables and the TUs of contaminants as Y variables. Before analysis, 15 toxicity parameters of the observed adverse effects were converted to the arcsine of their square roots to improve the homogeneity of variances and the normality of distributions, and the TUs of contaminants were logarithmically transformed. The comparisons and regressions were performed using SAS 9.1.3 software.

Results and Discussion

Chronic Sediment Toxicity

The five sediment samples from Tai Lake showed no acute mortality to *C. dilutus* (Fig. S2), and thus all of the samples were evaluated for chronic toxicity. The life-cycle toxicity testing was initiated with the newly hatched *C. dilutus* larvae and terminated at 47 days when the last midge emerged for 1 week. Water-quality parameters were monitored daily, and dissolved oxygen, pH, temperature, and conductivity were 5.6 ± 0.3 mg/L, 7.21 ± 0.04, 23 ± 1 °C, and 336 ± 18 µS/cm, respectively. Furthermore, the concentration of ammonia was measured at 0, 20, and 47 days and was approximately 0.2 mg/L. Results showed that water quality throughout the bioassays was in an acceptable range (USEPA 2000).

As shown in Fig. 1a, mean survival of the midges in control sediment was 78 ± 8 % at day 20, and this rate fulfilled the minimum criterion of 70 % of survival in sediment toxicity testing (USEPA 2000), thus indicating the effectiveness of the tests. Conversely, the survivorship of the midges in field sediments from Tai Lake was

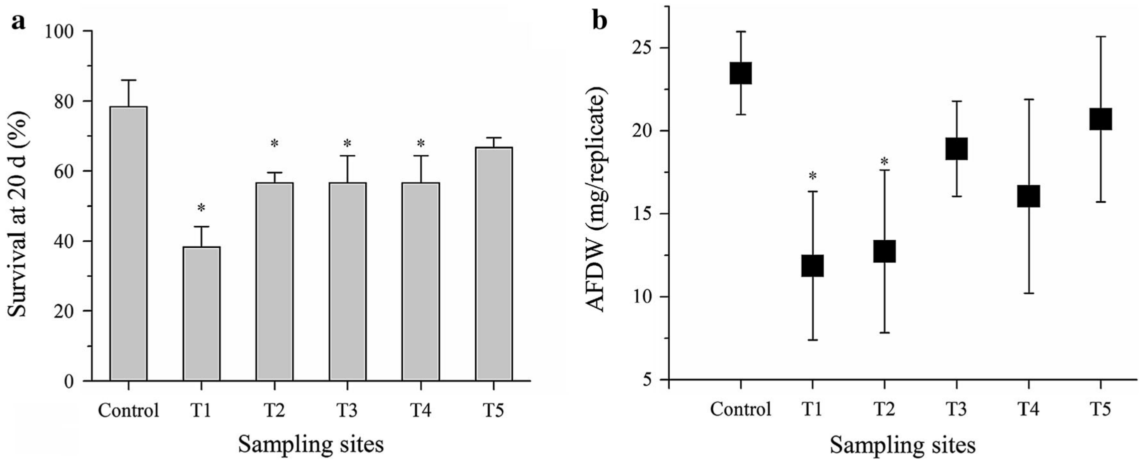

Fig. 1 Percent survival at day 20 (**a**) and AFDW (**b**) of *C. dilutus* exposed to sediments collected from Tai Lake (T1 through T5). Significant differences between test sediments and the control were determined by one-way ANOVA and are indicated by *asterisks* ($p < 0.05$). *Error bars* denote SD ($n = 3$)

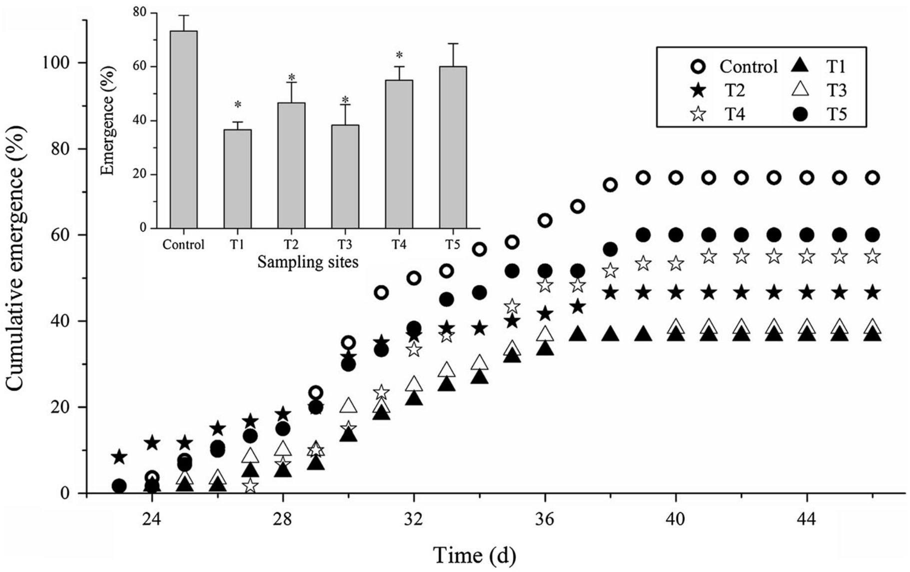

Fig. 2 Cumulative emergence of *C. dilutus* exposed to sediments collected from Tai Lake (T1 through T5). Significant differences of total emergence between test sediments and the control are presented in the *bar chart*. They were determined by one-way ANOVA and are indicated by *asterisks* ($p < 0.05$). *Error bars* denote SD ($n = 3$)

significantly decreased compared with the control ($p < 0.05$) with the exception of T5. The growth of an organism involves numerous biochemical, physiological, and behavioral processes, and the impairment of growth would lead to decreased fitness of the organisms and subsequently decreased population abundance (Sibley et al. 1997). As shown in Fig. 1b, The AFDWs of the midges in sediments T1 and T2 were less than one half of those of the control ($p < 0.05$), whereas AFDWs in the remaining three sediments were not significantly different from those of the control organisms.

Exposure to contaminated sediment also hindered the emergence of midges. As shown in Fig. 2, cumulative emergence of *C. dilutus* decreased from 73 ± 5 % in the control to 36 ± 3 % at site T1. Except for the midges in sediment T5, cumulative emergences in lake sediments were all significantly lower than that of the control ($p < 0.05$). In contrast, emergence time for the midges, which is the time required to achieve a predetermined percentage of emergence, were nearly the same among all treatments. It takes 40–50 days for *C. dilutus* to complete a life cycle under normal conditions (Gower and Buckland 1978), but this time might extend to >60 days for midges in contaminated sediments (Benoit et al. 1997). Nevertheless, the impact of chemical stressors on emergence time of the midges was not obvious in the sediments from Tai Lake with the longest time for midge emergence recorded at day 40 (Fig. 2). Therefore, the sediment samples from the north end of Tai Lake did not affect emergence time of *C. dilutus*, although cumulative emergences decreased.

Reproduction was chosen as another end point because it is not only sensitive to natural or anthropogenic stressors, it is also related to deterioration of the midges at the population level (Benoit et al. 1997). As shown in Fig. 3, fecundity of the midges decreased at site T1 (621 ± 191 eggs/female) relative to the control (872 ± 161 eggs/female) ($p < 0.05$), but no significant difference in fecundity was noted for others sites. Similar to previous studies (Du et al. 2013, 2014), egg hatchability was not sensitive to sediment-bound contaminants, and >91 % of eggs were hatched after midges were exposed to all sediments. In summary, except for site T5, field sediments from Tai Lake were chronically toxic—such as attenuated survivorship, decreased growth, impaired emergence, and low fecundity—to *C. dilutus*.

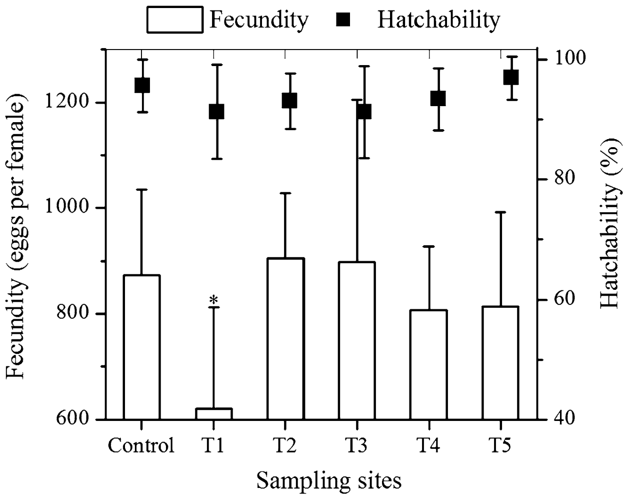

Fig. 3 Fecundity and hatchability of *C. dilutus* exposed to sediments collected from Tai Lake (T1 through T5). Significant differences between test sediments and the control were determined by ANOVA and are indicated by *asterisks* ($p < 0.05$). *Error bars* denote SD ($n = 3$)

Sediment Chemistry

POPs

In addition to the bioassays, contaminants of concern—including a series of POPs (PAHs, PCBs, and PBDEs), pesticides (OCPs, OPs, and PYRs), and metals—were also analyzed in the sediments from Tai Lake. The 16 PAHs in the priority list were all detected in sediment samples, and their total concentrations ranged from 504 to 889 ng/g dw (Table S3). Three- and four-ring PAHs dominated PAH compositions, accounting for 15–24 % and 35–42 % of total PAHs, respectively. These results were in accordant with recent studies in which concentrations of PAHs in Tai Lake sediments were from 179 to 1670 ng/g dw (Lei et al. 2014) and 209 to 1060 ng/g dw (Zhang et al. 2012a).

Compared with PAHs, concentrations of PCBs were extremely low. As shown in Table S4, the total concentrations of 27 PCBs in the five sediments were in a range of 0.56–1.81 ng/g dw, which is similar to a study in the same area [0.76–3.27 ng/g dw (Wang et al. 2011)]. Low concentrations of PCBs in China compared with those in North America (Krummel et al. 2005) were reasonable because historical use of PCBs was limited in China. Geographically, sediment T5 from the outlet of Wangyu River had the highest PCB concentration among the samples. It has been reported that PCB concentrations in Yangtze River were generally greater than those in Tai Lake, and relatively high PCB levels at site T5 might be a result of water diversion from Yangtze River to Tai Lake (Xu et al. 2000).

The total concentrations of eight PBDEs ranged from 38.6 to 87.8 ng/g dw, and BDE-209, the most abundant congener, ranged from 28.8 to 45.7 ng/g dw across sites (Table S5). This was in the same range of sediment concentrations of BDE-209 in Tai Lake reported in a previous study [9.68–144 ng/g dw (Zhou et al. 2012)].

Although POPs were detected in sediments from Tai Lake, their concentrations were far lower than the benchmark values for their risk, i.e., the equilibrium-partitioning sediment benchmarks for PAHs (12,403 µg/g OC) (USEPA 2003), the probable effect concentration (PEC) for PCBs (676 ng/g dw) (MacDonald et al. 2000), and the ecological screening values for penta-BDE (310 ng/g dw) and deca-BDE (>38,4000 ng/g dw) (Environment Canada 2006), thus suggesting that the risk from sediment-bound POPs to benthic organisms was negligible. Nevertheless, the potential of POPs to be bioaccumulated and biomagnified through the food web should not be overlooked (Yu et al. 2012).

Pesticides

Legacy OCPs and current-use OPs and PYRs were quantified as well. As shown in Table S6, p,p'-dichlorodiphenyltrichloroethane (p,p'-DDT) and endosulfan, and their metabolites, as well as hexachlorocyclohexanes (HCH) isomers were detectable in all lake sediments. Aldrin, dieldrin, endrin, and heptachlor were also occasionally found. The HCHs were the predominant OCPs, and β-HCH was the most abundant isomer of HCHs with concentrations of 1.00–6.07 ng/g dw. The concentrations of the most toxic isomer, γ-HCH, were from 0.04 ng/g dw in sediment T5 to 0.41 ng/g dw in sediment T1. The ratios of α-HCH to γ-HCH were <1 in all sites, whereas ratios of β-HCH/($\alpha + \gamma$)-HCH were >0.5 (11.2–37.1). The composition of HCH isomers implied that HCH residues in Tai Lake were primarily from the historical use of lindane, which had experienced long-time degradation in sediment (Willett et al. 1998). Instead, compositional patterns of DDT and its metabolites indicated recent possible input of DDT to Tai Lake. Although the ratios of (p,p'-DDE + p,p'-DDD)/p,p'-DDT were >0.5 in sediments T1 and T2, the values were <0.5 at the other three sites suggesting the presence of fresh DDT input (Rapaport et al. 1985). This result was consistent with that of a previous study, which explained that the fresh input of DDT in Tai Lake was due to the surface runoff from a typical alluvial plain of the Yangtze River Delta region, China (Hu et al. 2014).

Of the OCPs detected, β-HCH was the only one having concentrations greater than the USEPA freshwater sediment screening benchmark value of 5 ng/g dw (USEPA 2006) at sites T1, T2, and T4 (5.51, 6.07, and 5.56 ng/g dw, respectively). Although DDT concentrations in the sediments from Tai Lake were less than the benchmark value of 4.16 ng/g dw (USEPA 2006), attention should be paid to its ecological risk due to the possible fresh input and bioaccumulation potential.

Current-use pesticides (CUPs), e.g., OPs and PYRs, have become great threats to aquatic organisms because of their increasing use after legacy OCPs were banned (Li et al. 2014a). As shown in Table S7, chlorpyrifos and parathion-methyl were detectable in all sediments with mean concentrations of 1.52 and 0.72 ng/g dw, respectively. In addition, diazinon was found at greater than the RL in sediment T1. The input of OPs to the freshwater lakes in China was associated with their agricultural use in the watersheds (Wang et al. 2012b). Although detectable, the concentrations of chlorpyrifos were lower than its sediment-quality benchmarks (5.19 ng/g dw) (USEPA 2002).

Compared with the OPs, concentrations of sediment-bound PYRs were much lower in Tai Lake (Table S8). The total concentrations of PYRs were from 0.11 to 0.21 ng/g dw in the sediments, which is in accordance with a recent study in which 0.02–2.91 ng/g dw of PYRs were detected in Tai Lake (Fang et al. 2012). Permethrin and *lambda*-cyhalothrin were found in all sediments, whereas cypermethrin and esfenvalerate were detected in one sample at concentrations greater than the RL. The level and composition of PYRs in Tai Lake were distinct from those in urban areas in South China where 18–468 ng/g dw of PYRs were detected and where cypermethrin was the dominant PYR (Li et al. 2013). The concentrations of individual PYRs were lower than the PEC for permethrin, *lambda*-cyhalothrin, and cypermethrin (1960, 87, and 76 ng/g OC, respectively) (Moran et al. 2011), and this elucidated that ecological risk from sediment-bound CUPs in Tai Lake was limited.

Metals

As shown in Table S9, the total concentrations of seven metals ranged from 332 to 609 μg/g dw in the five sediments. The lowest concentration of metals was found in Gong Bay (sediment T4), whereas the highest was the outlet of Wangyu River to Yangze River (sediment T5); these results were similar to metal distributions in Tai Lake reported by Zhang et al. (2012b). In addition, Fu et al. (2013) also showed that the concentrations of sediment-bound metals in Yangtze River were much greater than those in Tai Lake. The highest metal concentration at site T5 in the current study might be related to water diversion from Yangtze River to Tai Lake as in the case of PCBs.

A comparison of metal concentrations in Tai Lake with the consensus-based PEC and TEC values (Table S9) (MacDonald et al. 2000) indicated that Ni and As were possibly risky with their concentrations greater than the PEC values at some sites. For instance, the concentration of Ni at sites T1 (58.6 μg/g dw) and T2 (50.2 μg/g dw) were greater than the PEC and between the PEC and the TEC, respectively, and the concentration of As at site T3 (34.5 μg/g dw) was slightly greater than its PEC.

Overall, POPs, pesticides, and metals were all frequently detected in the sediments collected from Tai Lake, but their concentrations were generally smaller than the values of sediment-quality guidelines with the exceptions of β-HCH, Ni, and As.

Identification of Potential Toxicity Contributors

To identify the possible contaminants causing chronic toxicity of Tai Lake sediments to the midges, TUs of individual contaminants were computed from their respective sediment concentrations and chronic EC$_{50}$ values (Table 1). When chronic-toxicity data were not available, the chronic EC$_{50}$ of a contaminant was estimated by dividing its median lethal concentration (LC$_{50}$) in acute toxicity testing by the acute-to-chronic ratio (ACR). Assuming concentration addition, the sum of the TUs of individual chemicals in the same class—including POPs (PAHs and PCBs), pesticides (OCPs, OPs and PYRs), and metals (As, Cd, Cr, Cu, Ni, Pb, and Zn)—was calculated. A TU of 0.5 was set as the threshold for substantial contribution to the toxicity (Weston et al. 2004).

Table 1 TUs of individual pesticides OC, OP, and PYR pesticides, and sum TUs of PAHs, PCBs, PBDEs, pesticides, metals, and all contaminants in sediments collected from Tai Lake (T1 through T5)

Contaminant	TU[a]				
	T1	T2	T3	T4	T5
p,p′-DDD	0.01	0.01	0.01	<0.01	<0.01
p,p′-DDE	<0.01	<0.01	<0.01	<0.01	<0.01
p,p′-DDT	<0.01	<0.01	0.01	0.01	0.01
Dieldrin	0.01	BRL	0.01	BRL	0.01
Endosulfan I	1.41	1.85	1.86	1.18	0.99
Endosulfan II	0.20	0.21	0.27	0.20	0.08
Endosulfan sulfate	0.10	0.22	0.42	0.50	0.60
Endrin	0.14	0.50	0.46	0.03	0.19
γ-HCH	1.44	0.44	0.90	0.75	0.06
Methoxychlor	BRL	0.01	BRL	0.01	0.01
ΣTU-OCP	3.30	3.22	3.92	2.67	1.93
Chlorpyrifos	0.65	0.70	0.67	0.34	0.14
Diazinon	0.01	BRL	BRL	BRL	BRL
Parathion-methyl	0.01	0.01	<0.01	<0.01	<0.01
ΣTU-OP	0.66	0.71	0.67	0.35	0.14
Cypermethrin	BRL	BRL	BRL	BRL	0.03
Esfenvalerate	0.01	BRL	BRL	0.01	BRL
lambda-Cyhalothrin	0.04	0.05	0.04	0.03	0.02
Permethrin	0.02	0.02	0.01	0.01	<0.01
ΣTU-PYR	0.08	0.07	0.05	0.06	0.07
ΣTU-pesticide	4.04	4.00	4.64	3.08	2.14
ΣTU-PAH	0.31	0.45	0.45	0.17	0.12
ΣTU-PCB	0.01	0.02	0.01	0.01	0.01
ΣTU-PBDE	0.04	0.02	0.02	0.01	0.02
ΣTU-Metal	1.59	1.46	1.49	1.21	1.62
ΣTU-all	5.98	5.94	6.60	4.47	3.90

BRL below reporting limit. The reporting limits for individual contaminants are presented in the supplementary material

Only the contaminants with at least one TU >0.01 are presented

[a] The TU was calculated from the concentration of contaminant in sediment and its EC$_{50}$ value. Sediment concentrations of individual contaminants and EC$_{50}$ values of PAHs, pesticides, and metals are presented in Tables S3 and S6 through S9 in the supplementary material. Due to the lack of EC$_{50}$ value, the PEC of 67.6 μg/g OC (MacDonald et al. 2000) was used to calculate TU of PCBs, and the ecological screening values for penta-BDE (310 ng/g dw) and deca-BDE (>38,4000 ng/g dw) were used to calculate TU of PBDEs (Environment Canada 2006)

TU of POPs

To estimate ΣTU of PAHs, the toxicity data of PAHs were first converted to benzo[a]pyrene (BaP) equivalents using the USEPA toxic equivalency factors (TEFs) (USEPA 1993). Then the EC_{50} of BaP for the emergence of *C. dilutus* in life-cycle toxicity testing (26.9 µg/g OC) was used to calculate the TU of PAHs (Du et al. 2014). As shown in Table 1, the ΣTU of PAHs ranged from 0.12 in sediment T5 to 0.45 in sediments T2 and T3, thus suggesting that PAHs may partially contribute to the observed toxicity but that the contribution was relatively low.

Because no toxicity data were available, TU values of PCBs and PBDEs were estimated by dividing sediment concentrations by the PEC value (MacDonald et al. 2000) and the ecological screening values (Environment Canada 2006), respectively. As a result, ΣTUs of PCBs and PBDEs were all <0.02 and <0.04 for all sediments, respectively. The negligible contribution of sediment-associated PCBs and PBDEs to the toxicity to the midges was also supported by the observations in a previous study. In this study, sediment samples from an electronic waste recycling site had PCB and PBDE concentrations hundreds times greater than those in Tai Lake, but they were not toxic to midges that were exposed to these sediments for 10 days (Mehler et al. 2011). Thus, it is reasonable to infer that PCBs and PBDEs in Tai Lake contributed little to sediment toxicity to the midges.

TU of Pesticides

As the most prevailing OCP, HCH was one of the main contributors to sediment toxicity (Table 1). γ-HCH was the only isomer that had attainable toxicity data for *C. dilutus* (Table S6). In addition, toxicity data for primary cultures of cerebellar granule cells suggested that γ-HCH was the most toxic isomer at 15–30 times greater potency than α- and σ-HCH, whereas β-isomer was relatively inactive (Pomés et al. 1993). Therefore, only γ-HCH was considered when calculating TU of HCH, thus implying a slight underestimation in the possible occurrence of HCH-TUs. Although most OCPs were banned in the 1980s, the use of endosulfan is still allowable in China resulting in its accumulation in the environment (Li et al. 2014b). Endosulfan and its metabolite contributed to the toxicity with TU values of 1.67–2.55. Endosulfan I is highly toxic to the midges and thus dominated the TU of endosulfans (0.99–1.86). Except for HCHs and endosulfans, other OCPs had TUs <0.5 at all sites implying their minimal contributions to the observed toxicity.

The TU of OPs ranged from 0.14 to 0.71 at all sites, and chlorpyrifos accounted for >95 % of OP TUs. The TUs of permethrin were calculated from its chronic EC_{50} value for the emergence of *C. dilutus* (0.84 µg/g OC) (Du et al. 2014). Because no chronic toxicity data are available for other PYRs, their chronic EC_{50} values were deducted by dividing their acute LC_{50} values by an ACR of 29.2, which was estimated from the toxicity data of permethrin. Sediment-bound PYRs were identified as being one of the principal contributors to toxicity to the midges in urban waterways of South China (Mehler et al. 2011). Conversely, PYRs were unlikely the contributors to the toxicity to *C. dilutus* in Tai Lake with the total TUs being between 0.05 and 0.08. Instead, chlorpyrifos was likely the CUP of a great concern due to its much greater TUs than those of other measured CUPs.

TU of Metals

The TUs of metals were calculated from the EC_{50} values of individual metals. As shown in Table 1, total-metal TUs ranged from 1.21 to 1.62 suggesting that metals also played a role in the chronic sediment toxicity to the midges in Tai Lake. In particular, As, Cr, and Ni contributed to the most of metal TUs.

Overall, the sum of TUs for all target contaminants at the five sites ranged from 3.9 to 6.6. The lowest TU value was found in sediment T5, and this was consistent with the results of the bioassay results, i.e., sediment T5 exhibited the least toxicity. Several chemicals, including PAHs, γ-HCH, endosulfans, chlorpyrifos, As, Cr, and Ni, were the plausible stressors to *C. dilutus*. To confirm whether chronic toxicity could be explained by these contaminants, the relationship between biological effects and chemical residues in sediment were evaluated by canonical correlation analysis.

Relationship Between Chronic Toxicity and TUs

Canonical correlation analysis was performed to attain a significant association between chronic toxicity and TUs of selected contaminants in the sediments. One set of variables (X_1–X_5) represented chronic effects including survival, emergence, growth, fecundity, and hatchability; the other set of variables (Y_1–Y_7) were the TUs of PAHs, endosulfans, γ-HCH, chlorpyrifos, As, Cr, and Ni, respectively. Five pairs of canonical correlations were obtained in this analysis, but only the first pair of canonical correlations (Corr [U_1, V_1]) was significant with a canonical coefficient (ρ_1) being 0.91 ($p < 0.01$). The original variables (X_i and Y_i) bearing canonical loading values >0.35 were selected because they provided a meaningful interpretation between U_1 and V_1 (Liu et al. 2009). As shown in Table 2, the canonical variables of biological effects mainly represented survival (0.79), emergence (0.90), and fecundity (0.41) because their canonical loading (in parentheses) are >0.35, whereas variables of TUs mainly represented γ-HCH (−0.81), chlorpyrifos (−0.75), Cr (−0.63), and Ni (−0.61). This showed that the long-term exposures to these four contaminants were probably associated with the adverse effects on survival, emergence, and fecundity in *C.*

Table 2 Canonical correlation between the two sets variables [chronic effects (X_1 through X_5) and log values of TU from sediment concentrations of contaminants (Y_1 through Y_7)]

Corr (U_1, V_1), $\rho_1 = 0.91$ ($p < 0.01$)[a]

Variable (X)	a_1[b]	Loading[c]	Variable (Y)	b_1[b]	Loading
Survival at 20 days (%)	0.19	**0.79**	PAHs	−4.5	−0.23
Emergence (%)	0.77	**0.90**	Endosulfans	1.21	−0.12
Growth (mg/replicate)	0.074	0.31	γ-HCH	−2.27	**−0.81**
Fecundity (eggs/female)	0.29	**0.41**	Chlorpyrifos	4.67	**−0.75**
Hatchability (%)	0.18	0.01	As	0.08	−0.31
			Cr	0.42	**−0.63**
			Ni	0.47	**−0.61**

[a] Corr (U_1, V_1) is the first pair of canonical correlation ($U_1 = a_{1,1}X_1 + a_{1,2}X_2 + \ldots + a_{1,5}X_5$, $V_1 = b_{1,1}Y_1 + b_{1,2}Y_2 + \ldots + b_{1,7}Y_7$), and ρ_1 is the coefficient of the first pair of canonical correlation

[b] a_1 and b_1 are standardized canonical coefficients

[c] Loading is canonical loadings: Loadings >0.35 are highlighted in bold. These were used to select variables believed to give a meaningful interpretation between the new pair of variables (Liu et al. 2009)

dilutus. In contrast, the contributions from PAHs, endosulfans and As were relatively minimal because their canonical loading are <0.35.

Conclusions

Although sediment samples from Tai Lake in China were not acutely lethal to *C. dilutus*, adverse effects after chronic exposure were observed for most sediments. To better understand sediment risk in freshwater lakes, therefore, it is desirable to evaluate chronic toxicity to benthic organisms, which are more sensitive and environmentally relevant. Contaminants that were potentially responsible for sediment toxicity were screened by a TU approach and further identified by assessing the relationship between chronic toxicity and the occurrence of contaminants using canonical correlation analysis. Two pesticides (HCH and chlorpyrifos) and two metals (Cr and Ni) in sediments from Tai Lake were identified as being potential contributors to the impairments of survival, emergence, and fecundity of *C. dilutus*.

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References

Belden JB, Gilliom RJ, Lydy MJ (2007) How well can we predict the toxicity of pesticide mixtures to aquatic life? Integr Environ Assess Manag 3(3):364–372

Benoit DA, Sibley PK, Juenemann JL, Ankley GT (1997) *Chironomus tentans* life-cycle test: design and evaluation for use in assessing toxicity of contaminated sediments. Environ Toxicol Chem 16(6):1165–1176

Du J, Pang J, You J (2013) Bioavailability-based chronic toxicity measurements of permethrin to *Chironomus dilutus*. Environ Toxicol Chem 32(6):1403–1411

Du J, Li Y, Huang ZC, You J (2014) Chronic toxicity thresholds for sediment-associated benzo[a]pyrene in the midge (*Chironomus dilutus*). Arch Environ Contam Toxicol 66(3):370–378

Duan HT, Ma RH, Xu XF, Kong FX, Zhang SX, Kong WJ et al (2009) Two-decade reconstruction of algal blooms in China's Lake Taihu. Environ Sci Technol 43(10):3522–3528

Environment Canada (2006) Ecological screening assessment report on polybrominated diphenyl ethers (PBDEs). Environment Canada, Ottawa, ON

Fang S, Chen P, Bian J, Zhong W, Zhu L (2012) Levels and toxicity assessment of pyrethroids in the surface sediments of Taihu Lake and Liaohe River. Acta Sci Circ 32(10):2600–2606

Förstner U (2004) Sediments—resource or waste. J Soil Sed 4(1):3

Fu J, Hu X, Tao X, Yu H, Zhang X (2013) Risk and toxicity assessments of heavy metals in sediments and fishes from the Yangtze River and Taihu Lake, China. Chemosphere 93(9):1887–1895

Gower AM, Buckland PJ (1978) Water-quality and occurrence of *Chironomus riparius* meigen (diptera-chironomidae) in a stream receiving sewage effluent. Freshw Biol 8(2):153–164

Hu W, Huang B, Zhao Y, Sun W, Gu Z (2014) Distribution, sources and potential risk of HCH and DDT in soils from a typical alluvial plain of the Yangtze River Delta region, China. Environ Geochem Health 36(3):345–358

Krummel EM, Gregory-Eaves I, Macdonald RW, Kimpe LE, Demers MJ, Smol JP et al (2005) Concentrations and fluxes of salmon-derived polychlorinated biphenyls (PCBs) in lake sediments. Environ Sci Technol 39(18):7020–7026

Lei B, Kang J, Wang X, Yu Y, Zhang X, Wen Y et al (2014) The levels of PAHs and aryl hydrocarbon receptor effects in sediments of Taihu Lake, China. Environ Sci Pollut R 21(10):6547–6557

Li H, Sun B, Lydy MJ, You J (2013) Sediment-associated pesticides in an urban stream in Guangzhou, China: implication of a shift in pesticide use patterns. Environ Toxicol Chem 32(5):1040–1047

Li H, Zeng EY, You J (2014a) Mitigating pesticide pollution in China requires law enforcement, farmer training, and technological innovation. Environ Toxicol Chem 33(4):963–971

Li P, Wang Y, Huang W, Yao H, Xue B, Xu Y (2014b) Sixty-year sedimentary record of DDTs, HCHs, CHLs and endosulfan from emerging development gulfs: a case study in the Beibu Gulf, South China Sea. Bull Environ Contam Toxicol 92(1):23–29

Liu J, Drane W, Liu XF, Wu TJ (2009) Examination of the relationships between environmental exposures to volatile organic compounds and biochemical liver tests: application of canonical correlation analysis. Environ Res 109(2):193–199

Lu G, Yang X, Li Z, Zhao H, Wang C (2013) Contamination by metals and pharmaceuticals in northern Taihu Lake (China) and its relation to integrated biomarker response in fish. Ecotoxicology 22(1):50–59

Ma Z, Chen K, Yuan Z, Bi J, Huang L (2013) Ecological risk assessment of heavy metals in surface sediments of six major chinese freshwater lakes. J Environ Qual 42(2):341–350

MacDonald DD, Ingersoll CG, Berger TA (2000) Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Arch Environ Contam Toxicol 39(1):20–31

Mehler WT, Li H, Lydy MJ, You J (2011) Identifying the causes of sediment-associated toxicity in urban waterways of the Pearl River Delta, China. Environ Sci Technol 45(5):1812–1819

Moran PW, Calhoun DL, Nowell LH, Kemble NE, Ingersoll CG, Hladik ML, et al (2011) Contaminants in stream sediments from seven US metropolitan areas: Data summary of a national pilot study. United States Geological Survey Scientific Investigations Report 5092:22

Pomés A, Rodríguez-Farré E, Suñol C (1993) Inhibition of *t*-[^{35}S] butylbicyclophosphorothionate binding by convulsant agents in primary cultures of cerebellar neurons. Dev Brain Res 73(1):85–90

Rapaport RA, Urban NR, Capel PD, Baker JE, Looney BB, Eisenreich SJ et al (1985) New DDT inputs to North America: atmospheric deposition. Chemosphere 14(9):1167–1173

Sibley PK, Benoit DA, Ankley GT (1997) The significance of growth in *Chironomus tentans* sediment toxicity tests: relationship to reproduction and demographic endpoints. Environ Toxicol Chem 16(2):336–345

Sun B, Wang F, Li H, You J (2015) Occurrence and toxicity of sediment-associated contaminants in Guangzhou College City and its adjacent areas: the relationship to urbanization. Arch Environ Contam Toxicol 68(1):124–131

United States Environmental Protection Agency (1993) Provisional guidance for quantitative risk assessment of polycyclic aromatic hydrocarbons. EPA/600/R-93/089, USEPA, Washington, DC

United States Environmental Protection Agency (2000) Methods for measuring the toxicity and bioaccumulation of sediment-associated contaminants with freshwater invertebrates. EPA600/R-99/064, USEPA, Washington, DC

United States Environmental Protection Agency (2002) Interim reregistration eligibility decision for chlorpyrifos. EPA 738-R-01-007, USEPA, Washington, DC

United States Environmental Protection Agency (2003) Procedures for the derivation of equilibrium partitioning sediment benchmarks (ESBs) for the protection of benthic organisms: PAH mixtures. EPA/600/R-02/013, USEPA, Washington, DC

United States Environmental Protection Agency (2006) EPA region III BTAG freshwater sediment screening benchmarks. USEPA, Washington

Wang C, Lu G, Wang P, Wu H, Qi P, Liang Y (2011) Assessment of environmental pollution of Taihu Lake by combining active biomonitoring and integrated biomarker response. Environ Sci Technol 45(8):3746–3752

Wang X, Xu J, Guo C, Zhang Y (2012a) Distribution and sources of organochlorine pesticides in Taihu lake, China. Bull Environ Contam Toxicol 89(6):1235–1239

Wang JZ, Li HZ, You J (2012b) Distribution and toxicity of current-use insecticides in sediment of a lake receiving waters from areas in transition to urbanization. Environ Pollut 161:128–133

Weston DP, You J, Lydy MJ (2004) Distribution and toxicity of sediment-associated pesticides in agriculture-dominated water bodies of California’s Central Valley. Environ Sci Technol 38(10):2752–2759

Willett KL, Ulrich EM, Hites RA (1998) Differential toxicity and environmental fates of hexachlorocyclohexane isomers. Environ Sci Technol 32(15):2197–2207

Xu SF, Jiang X, Dong YY, Sun C, Feng JF, Wang LS et al (2000) Polychlorinated organic compounds in Yangtse River sediments. Chemosphere 41(12):1897–1903

Yu YX, Zhang SH, Huang NB, Li JL, Pang YP et al (2012) Polybrominated diphenyl ethers and polychlorinated biphenyls in freshwater fish from Taihu Lake, China: their levels and the factors that influence biomagnification. Environ Toxicol Chem 31(3):542–549

Zhang Y, Shi GL, Guo CS, Xu J, Tian YZ, Feng YC et al (2012a) Seasonal variations of concentrations, profiles and possible sources of polycyclic aromatic hydrocarbons in sediments from Taihu Lake, China. J Soil Sed 12(6):933–941

Zhang Y, Hu X, Yu T (2012b) Distribution and risk assessment of metals in sediments from Taihu Lake, China using multivariate statistics and multiple tools. Bull Environ Contam Toxicol 89(5):1009–1015

Zhou P, Lin K, Zhou X, Zhang W, Huang K, Liu L et al (2012) Distribution of polybrominated diphenyl ethers in the surface sediments of the Taihu Lake, China. Chemosphere 88(11):1375–1382