

Occurrence and Toxicity of Sediment-Associated Contaminants in Guangzhou College City and Its Adjacent Areas: The Relationship to Urbanization

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Abstract Guangzhou College City in the southeast of Guangzhou, China, became a home to 10 universities in 2003 after a largely agricultural past. The city has since experienced rapid urbanization with limited development of adjacent areas. Twenty-one sediment samples were collected in the city and its adjacent areas to evaluate the influence of urbanization in different functional zones on sediment quality in local waterways. Sediment toxicity was assessed by 10-day toxicity tests using two benthic invertebrates, *Chironomus dilutus* and *Hyaella azteca*. In addition, various organic contaminants—including current-use pesticides (pyrethroids and organophosphate insecticides) and polycyclic aromatic hydrocarbons—were analyzed, and a toxic unit (TU) approach was applied to identify possible toxicity contributors. In general, 38 and 4.8 % of the sediments exhibited acute toxicity to *C. dilutus* and *H. azteca*, respectively, with 9.5 % of the samples resulting in 100 % mortality to *C. dilutus*. Distribution analysis showed that the rural industrial area, which is south of the city, had the greatest contaminant concentrations and greatest toxicity to both organisms compared with the other areas. Pyrethroids, especially cypermethrin, appeared to contribute the most to the observed toxicity,

yet the lack of relationship between the toxicity and TU of pyrethroids may reflect toxicity associated with other contaminants.

China has experienced rapid urbanization in recent decades. For instance, as the largest city in the Pearl River Delta (PRD) and one of the most developed economic centers in China, Guangzhou has a population, an urbanization rate, and a regional gross domestic product of 12.7 million, 83.8 %, and 1,075 billion RMB in 2010, respectively (http://www.gzstats.gov.cn/gzsq/201112/t20111229_27422.htm).

Severe deterioration of urban waterways has occurred in tandem with the urbanization and water quality was noted to be related to local development status, i.e., a higher urbanization rate caused more serious water pollution (Defu et al. 2014; Tang et al. 2005; Zhu et al. 2011). Various pollutants—including organics, ammonia, and metals—contributed to the degradation of water quality in urban areas (Hong et al. 2012; Zhu et al. 2002). In a study of pesticide distribution in the PRD, Li et al. (2011) reported that urbanization increased the occurrence of current-use pesticides (CUPs), e.g., pyrethroid and organophosphate (OP) pesticides, in urban waterways. Furthermore, CUPs were identified as the main toxicity contributors to benthic organisms in this region (Li et al. 2013a; Mehler et al. 2011). The input of pyrethroid residues into aquatic ecosystems due to urbanization was also confirmed by assessing the distribution and toxicity of CUPs in sediment samples from a lake that received waters from the areas in transition to urbanization (Wang et al. 2012). A significant relationship between the distribution of pyrethroids and typical urban-oriented contaminants (PAHs and linear alkylbenzenes) implied that urban runoff

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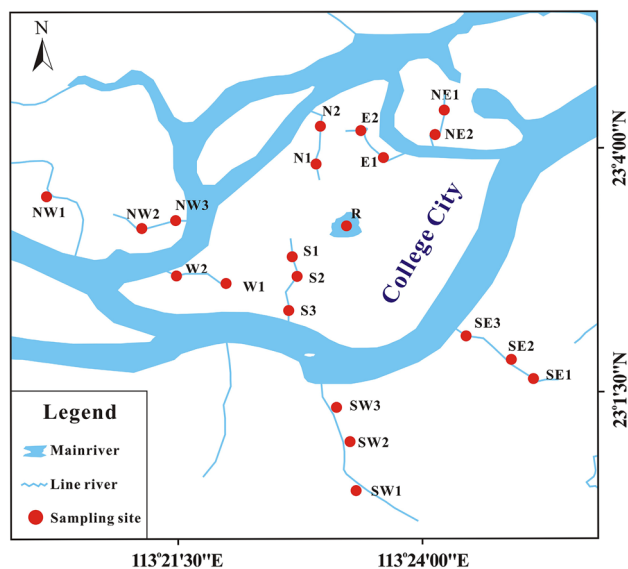


Fig. 1 Map of the sampling sites in Guangzhou College City and its adjacent areas

might be an important source for pyrethroid residues in the lake (Wang et al. 2012).

Although the adverse impact of urbanization on aquatic ecosystems is evident, continuous urbanization is inevitable in China and other developing countries. Therefore, the question is how to keep sustainable growth in the process of urbanization at minimized environmental cost. Urbanization could occur with or without well-defined plans, resulting in the emergence of various functional zones in the developing urban areas. To evaluate the linkages between the patterns of urbanization, types of functional zones and ecological risk would shed a light on future studies on environmental protection during urbanization.

The objective of the current study was to evaluate the impacts of different land-use activities, or functional zones, in Guangzhou College City and adjacent areas on sediment toxicity in local waterways. Three aims were addressed as follows: (1) assess the acute toxicity of sediment samples collected in the College City and its adjacent areas to two benthic invertebrates, *Chironomus dilutus* and *Hyalella azteca*; (2) evaluate possible toxicity contributions using a TU approach by analyzing hydrophobic organic contaminants in sediments; and (3) investigate spatial distribution of sediment toxicity and contaminant residues in different functional zones.

Materials and Methods

Sampling Site and Sediment Collection

Guangzhou College City is situated on an island surrounded by the Pearl River. This area was formerly

farmlands and in 2003 quickly transitioned to an urban area with 10 universities. The city is now made up of urban, agricultural, and rural industrial areas (Fig. S1 in the Supplementary Material [SM]). This college city was therefore an ideal location to study the environmental impacts of different developmental modes of urbanization on local aquatic ecosystems.

In total, 21 sediment samples were collected from streams in Guangzhou College City and its adjacent areas (Fig. 1). Although the center of the island of the college city continued developing into a well-organized urban residual area after the 10 universities moved into this island in 2003, the surrounding areas gradually developed into different functional zones—including an ecological park, rural industrial areas, and suburban villages—with agricultural lands without any planning (Fig. S1 in the SM).

The coordinates and brief descriptions of the sampling sites and the total organic carbon (TOC) contents of the sediments are listed in Table S1 in the SM. Ten sediments collected in College City were sampled in the streams close to the universities, which mainly receive domestic sewage and urban runoff. Among them, a sediment sample collected from Central Lake inside of College City was used as the reference sediment. Six sediments were collected in rural industrial areas that were located in the southwest and southeast of College City. Three sediments were collected in Yingzhou Ecological Park in the northwest of College City, and the remaining two sediments were collected in the suburban villages with agricultural lands in the northeast of College City (Fig. 1). The top 5 cm of surface sediment was collected using a spade shovel by wading into the streams. The sediments were sieved through a 2-mm stainless sieve on site to remove rocks and organic debris. After sampling, sediment samples were immediately transported to the laboratory at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIGCAS), and stored at -20 and 4 °C in the dark for chemical analysis and toxicity testing, respectively. In addition, a sediment sample collected from a drinking water reservoir in Conghua (CH), which is close to Guangzhou, was used as control sediment. Preliminary tests showed that the CH sediment sample was not acutely toxic to *C. dilutus* and *H. azteca*, and no target compounds were detected at concentrations greater than the reporting limits (RLs) in this sediment.

Toxicity Testing

Ten-day sediment acute toxicity testing was performed using *C. dilutus* and *H. azteca* in six replicates (USEPA 2000). The organisms were cultured at GIGCAS in accordance with USEPA protocol (USEPA 2000). After sediment was homogenized using a stainless steel spatula

driven by a drill for 4 h, 70 g of wet sediment was distributed into each 400-ml beaker, and then 300 ml of reconstituted water was added as overlying water. After allowing the sediment to settle overnight, 10 third-instar *C. dilutus* or 7–14 day-old *H. azteca* were randomly added into each beaker. Control tests for both species using CH sediment were performed simultaneously. The toxicity tests were performed in an automated water-delivery system with temperature and photocycle being set at 23 ± 1 °C and 16–8 h of light and dark, respectively. Overlying water was changed twice daily with approximately 150 ml of reconstituted water being renewed each time. Water parameters—including pH, temperature, conductivity, and dissolved oxygen—were monitored daily before water change. Concentrations of ammonia in overlying water were measured at the beginning and end of the testing. The organisms were fed once with 1 ml of grounded fish food at 6 g/l/beaker/day. At the termination of the tests, survived organisms were counted by sieving the organisms from the sediments using a 500- μ m sieve.

Chemical Analysis

A series of hydrophobic organic contaminants—including nine pyrethroids, five OP pesticides, and 15 PAHs—were analyzed in the current study. A list of the target compounds are listed in Table S2 in the SM. Sediment samples were extracted with a mixture of acetone and hexane using a CW-2000 ultrasound assisted microwave extractor (Xintuo Company, Shanghai, China) and cleaned using SPE cartridges or self-packed columns. Target compounds were analyzed on a Shimadzu QP-2010-plus gas chromatographer/mass spectrometer (Shimadzu, Japan). Detailed descriptions of chemical and reagents, analytical methods for sediment extraction, cleanup and instrumental analysis, and procedures of quality assurance and quality control are presented in the SM. The TOC contents of the sediments were analyzed using a C230 carbon determinator (Leco, USA) after removing the inorganic carbonates with 1 mol/l of HCl.

Data Analysis

A TU approach was used to assess the contribution of each contaminant to the observed sediment toxicity based on the measured chemical concentrations in sediment and toxicity benchmark of the corresponding chemical (Eq. 1):

$$TU = \frac{\text{Contaminant concentration in sediment}}{\text{LC50 or sediment benchmark}} \quad (1)$$

The median lethal concentrations (LC50) of pesticides were collected from the literature and are listed in Table S3 in the SM. The LC50 values for PAHs to the test species

were not available; therefore, equilibrium sediment benchmarks (ESBs; USEPA 2004) and a threshold effect concentration (TEC) value of 290 μ g/g OC on the basis of summed PAH concentrations (Swartz 1999) were applied to estimate the contribution of PAHs to sediment toxicity, and the ESB values are listed in Table S4 in the SM. The total toxicity contribution was calculated based on concentration addition.

Sediment toxicity was assessed by comparing site sediments with the control sediment using Student *t* tests (SAS version 8.02, SAS Institute, USA), and a significant difference ($p < 0.05$) indicated that the sediment was acutely toxic to the organisms.

Results and Discussion

Sediment Toxicity

Water quality during the toxicity testing was within USEPA guidelines (USEPA 2000). Water temperature, pH, conductivity, and dissolved oxygen concentrations were 23.6 ± 1.0 °C, 7.6 ± 0.2 , 329 ± 36 μ S/cm, and 5.6 ± 2.0 mg/l, respectively. Sediment mortality to *C. dilutus* and *H. azteca* are presented in Fig. 2. Both control and reference sediments caused 3.3 ± 5.2 % mortality to *C. dilutus*. Compared with the control, 8 of 21 site sediments exhibited acute toxicity to *C. dilutus* with 2 of them causing 100 % mortality (Fig. 2). The mortality of the control and reference sediments to *H. azteca* was 8.3 ± 13 and 3.3 ± 5.2 %, respectively. Only one sediment sample exhibited significant acute toxicity to *H. azteca* compared with the controls, and this sediment (site SE2) was collected in the southeast of College City (rural industrial areas; Fig. 2 and Fig. S1 in the SM).

Geographically, most of the sediments collected from College City were not acutely toxic to *C. dilutus* compared with the controls, except for 3 of the 10 sediments (sites S1, S3, and W1), which caused 38.3, 38.3, and 96.7 % mortality, respectively. Comparatively, sediments collected from the southeast and southwest of College City, where rural industrial factories are located, exhibited greater mortality to *C. dilutus* with 83 % of sediments (5 of 6) being acutely toxic. Sediments collected from the northeast and northwest of College City, where a suburban community with patches of vegetable lands and Yingzhou Ecological Park are located, respectively, were not acutely toxic to *C. dilutus*. As shown in Fig. 3, sediment toxicity was compared among the four functional zones, and the results suggested that sediments collected in the rural industrial area (the southeast and southwest regions) caused significantly greater mortality to *C. dilutus* ($p < 0.01$) than that in the other three functional zones. Although only a

Fig. 2 Mortality of *C. dilutus* and *H. azteca* exposed to sediments collected from Guangzhou College City and its adjacent areas. Stars and triangles indicate that sediment toxicity to *C. dilutus* and *H. azteca* was significantly different from the controls, respectively. Letters “a” and “b” indicate that toxicity of the sediment to the two test species was significantly different ($p < 0.05$)

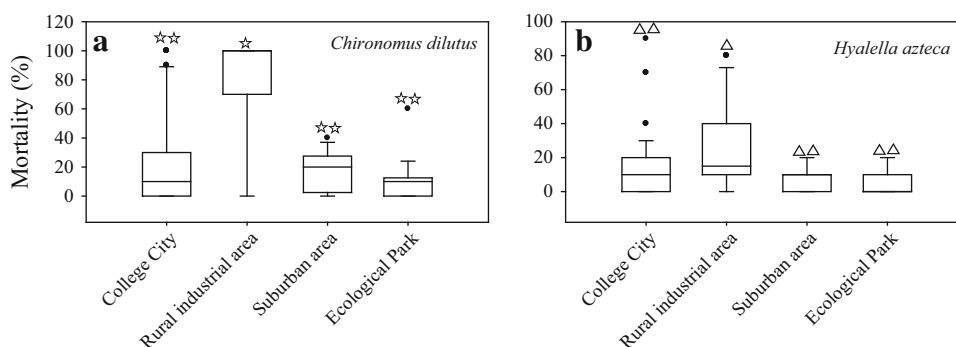
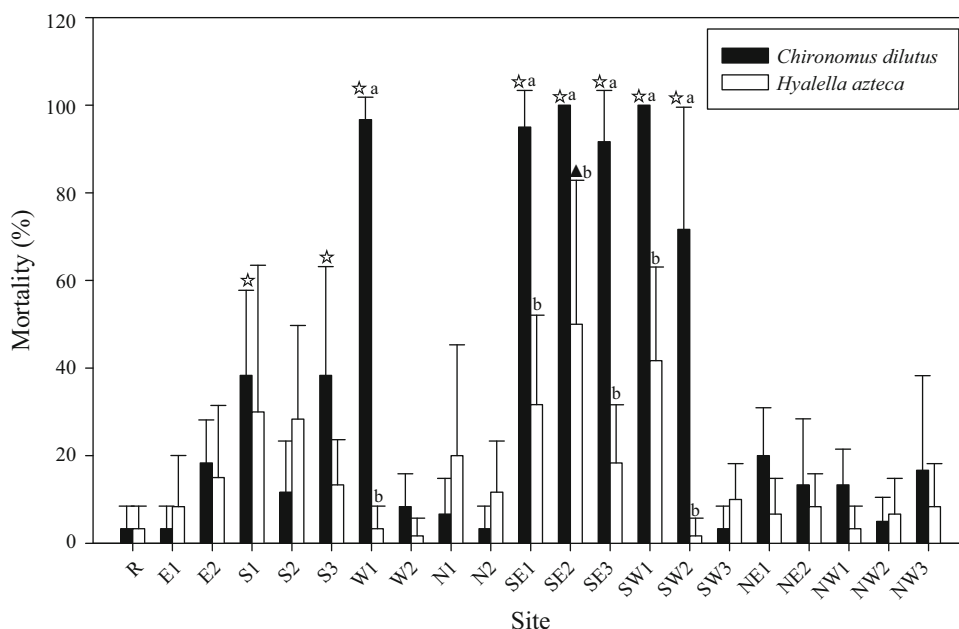


Fig. 3 Box-plot of mortality (%) to *C. dilutus* (a) and *H. azteca* (b) in sediments from different functional zones of College City and its adjacent areas. The two dots represent the greatest and the lowest mortality; the three lines of the box represent 25, 50, and 75 % of the

mortality; and the bars represent the SDs. The number of stars and triangles indicates that sediment toxicity to *C. dilutus* and *H. azteca* was significantly different among functional zones, respectively ($p < 0.05$)

sediment collected in the rural industrial area was acutely toxic to *H. azteca*, average mortality of sediments collected in the rural industrial area was significantly greater than in sediments collected in other three functional zones ($p < 0.05$) (Fig. 3).

Sediment toxicity in the current study was compared with that found by other studies performed in the PRD, China, and the United States, and the results are listed in Table 1. Overall, sediments collected from College City had significantly lower toxicity to benthic organisms than sediments collected from other urban areas in Guangzhou (Li et al. 2013a, b; Mehler et al. 2011), Dongguan, and Shenzhen (Mehler et al. 2011) in the PRD. Sediments collected from the rural industrial area, which is located in the south of College City, had comparable acute toxicity to *C. dilutus* as other urban sites in the PRD (Li et al. 2013a;

Mehler et al. 2011). Regarding sediment toxicity to *H. azteca*, sediments collected from College City and its adjacent areas showed significantly lower toxicity than sediments from urban and agricultural areas in Illinois and California, USA (Ding et al. 2010; Weston et al. 2005).

Toxicity Contributors

Five pyrethroids (bifenthrin, cyhalothrin, cypermethrin, esfenvalerate, and permethrin) and three OP pesticides (chlorpyrifos, parathion-methyl, and terbufos) were detected in the sediments at concentrations greater than the RLs in at least one sediment sample with sum concentrations of pyrethroids and OP pesticides being 0.05–4.96 $\mu\text{g/g}$ OC and $< \text{RL}$ to 0.29 $\mu\text{g/g}$ OC, respectively (Table S3 in the SM). The PAHs were detected in all samples with sum

Table 1 Comparison of sediment toxicity to *C. dilutus* and *H. azteca* in the current study compared with that of previous studies

| Sampling region | Site description | Sediment caused acute toxicity (%) to | | Sediment caused 100 % mortality (%) to | | References |
|---|--|---------------------------------------|------------------|--|------------------|----------------------|
| | | | | | | |
| | | <i>C. dilutus</i> | <i>H. azteca</i> | <i>C. dilutus</i> | <i>H. azteca</i> | |
| California, USA | Residential area | – | 86 | – | 41 | Weston et al. (2005) |
| Illinois, USA | Urban | – | 58 | – | 0 | Ding et al. (2010) |
| Illinois, USA | Agricultural | – | 0 | – | 0 | Ding et al. (2010) |
| PRD, China | Cities (Guangzhou, Dongguan, and Shenzhen) | 86 | – | 50 | – | Mehler et al. (2011) |
| College City in Guangzhou, China | Urban | 20 | – | 0 | – | Mehler et al. (2011) |
| Guangzhou, China | Urban | 94 | 81 | 81 | 38 | Li et al. (2013a, b) |
| College City and its adjacent areas in Guangzhou, China | Urban, agriculture, industrial | 38 | 4.7 | 9.5 | 0 | Current study |
| College City in Guangzhou, China | Urban | 30 | 0 | 0 | 0 | Current study |
| Rural industrial area in Guangzhou, China | Rural industrial | 83 | 17 | 33 | 0 | Current study |
| Surburb in Guangzhou, China | Yingzhou Ecological Park and suburb villages | 0 | 0 | 0 | 0 | Current study |

concentrations of 6.62–39.3 $\mu\text{g/g}$ OC (Table S4 in the SM). Mean concentration of total pyrethroids in the sediment samples collected from the rural industrial area (1.86 $\mu\text{g/g}$ OC) was approximately 2.5 times greater than that in the sediment samples from the other three functional zones. Specifically, variation in permethrin concentrations was the main reason for the significant difference in sediment concentrations of total pyrethroids among different functional zones with mean sediment concentration of permethrin in the rural industrial area being 4.5 times greater than that from other functional zones.

Furthermore, TUs of the target compounds were calculated to assess their contributions to the observed toxicity to *C. dilutus* and *H. azteca* (Table 2). The mean TUs of the detected pyrethroids were 0.34 and 1.23 for *C. dilutus* and *H. azteca*, respectively. The TU of individual pyrethroids is listed in Table S5 in the SM. Cypermethrin accounted for the greatest part of summed TUs of pyrethroids with mean percentages being 82 and 80 % to *C. dilutus* and *H. azteca*, respectively. The TUs for OP pesticides were < 0.1 to both species, thus suggesting their small contributions to sediment toxicity (Table 2). Other than pesticides, TUs of summed PAHs were calculated using two benchmarks (TEC and ESB), and the TUs were < 0.15. Overall, pyrethroids accounted for the most of TUs. These results are consistent with our previous studies on sediment toxicity in the PRD, i.e., pyrethroids were one of the main toxicity contributors to benthic organisms, whereas the contributions of OP pesticides and PAHs were negligible compared with that of pyrethroids (Mehler et al. 2011).

To identify the contribution of sediment-bound pyrethroids to benthic organisms, TUs of pyrethroids in the

sediments collected in study area were correlated with observed toxicity in the bioassays. No significant relationships were observed for *C. dilutus* or *H. azteca*. In contrast, a significant correlation (observed toxicity = $0.93 \text{ TU} + 0.41$, $r^2 = 0.53$, $p < 0.01$) was noted between pyrethroid TUs and the observed toxicity to *C. dilutus* when data from the current study were plotted together with those in previous studies in the PRD (Li et al. 2013a; Mehler et al. 2011) (Fig. 4), thus suggesting that pyrethroids might contribute to the sediment toxicity to *C. dilutus*.

Distribution Among Different Functional Zones

Sediments collected from the south of Guangzhou College City (rural industrial areas) exhibited greater toxicity to both organisms than sediments from College City and its northern part. The rural industrial area is a complex region with both agricultural and industrial practices, and its unruly economic development may be one reason for its relatively greater sediment toxicity compared with that in other zones. The increase of rural industries significantly contributed to China's economic growth after the economic reform in 1978 in this country, but it has also become a threat to the environment. Being small enterprises, rural industries generally lack wastewater-treatment facilities, and its growth was neither planned nor anticipated. Wang et al. (2008) reported that most of the untreated discharge in China comes from rural industries and that water pollution related to rural industrialization was a serious problem. This explained the greatest sediment toxicity observed in rural industrial area among all functional zones (Fig. 3).

Table 2 TUs of PAHs, pyrethroids, and OP pesticides in sediments collected from College City and its adjacent area to *C. dilutus* and *H. azteca*

| Site | PAHs | | TU to <i>C. dilutus</i> ^a | | | TU to <i>H. azteca</i> ^a | | | Contribution of TU of pyrethroids to \sum TU (%) | |
|---------|------------------|------------------|--------------------------------------|------|-----------|-------------------------------------|------|-----------|--|------------------|
| | ESB ^b | TEC ^c | PYRE | OP | \sum TU | PYRE | OP | \sum TU | <i>C. dilutus</i> | <i>H. azteca</i> |
| R | 0.02 | 0.04 | 0.01 | 0.00 | 0.05 | 0.02 | 0.03 | 0.09 | 20.2 | 25.8 |
| E1 | 0.03 | 0.07 | 0.20 | 0.00 | 0.27 | 0.76 | 0.01 | 0.84 | 74.1 | 90.8 |
| E2 | 0.02 | 0.06 | 0.32 | BRL | 0.38 | 1.23 | BRL | 1.29 | 84.2 | 95.3 |
| S1 | 0.03 | 0.07 | 0.44 | 0.00 | 0.51 | 1.62 | 0.01 | 1.70 | 85.7 | 95.3 |
| S2 | 0.02 | 0.05 | 0.08 | 0.00 | 0.13 | 0.29 | 0.01 | 0.34 | 60.5 | 83.7 |
| S3 | 0.03 | 0.08 | 0.53 | 0.02 | 0.63 | 2.09 | 0.03 | 2.21 | 84.2 | 94.9 |
| W1 | 0.02 | 0.06 | 1.51 | 0.01 | 1.58 | 5.51 | 0.03 | 5.60 | 95.3 | 98.4 |
| W2 | 0.01 | 0.02 | 0.03 | 0.00 | 0.05 | 0.09 | 0.00 | 0.11 | 56.9 | 79.4 |
| N1 | 0.02 | 0.05 | 0.39 | 0.00 | 0.45 | 1.44 | 0.00 | 1.49 | 88.1 | 96.4 |
| N2 | 0.03 | 0.06 | 0.20 | 0.00 | 0.27 | 0.75 | 0.01 | 0.82 | 76.2 | 91.6 |
| SE1 | 0.02 | 0.05 | 0.21 | 0.00 | 0.26 | 0.73 | 0.00 | 0.79 | 81.1 | 93.0 |
| SE2 | 0.02 | 0.06 | 0.14 | 0.00 | 0.20 | 0.46 | 0.01 | 0.53 | 68.5 | 87.2 |
| SE3 | 0.02 | 0.05 | 0.38 | 0.00 | 0.43 | 1.33 | 0.01 | 1.39 | 88.3 | 95.9 |
| SW1 | 0.05 | 0.14 | 0.90 | 0.03 | 1.07 | 3.13 | 0.05 | 3.33 | 84.1 | 94.2 |
| SW2 | 0.01 | 0.04 | 0.27 | 0.00 | 0.31 | 0.96 | 0.01 | 1.01 | 87.1 | 95.2 |
| SW3 | 0.03 | 0.06 | 0.48 | BRL | 0.54 | 1.65 | BRL | 1.71 | 88.8 | 96.5 |
| NE1 | 0.01 | 0.03 | 0.48 | 0.00 | 0.52 | 1.74 | 0.01 | 1.78 | 93.8 | 98.0 |
| NE2 | 0.03 | 0.09 | 0.17 | 0.00 | 0.26 | 0.65 | 0.00 | 0.74 | 65.7 | 87.3 |
| NW1 | 0.03 | 0.07 | 0.14 | 0.01 | 0.21 | 0.50 | 0.02 | 0.59 | 64.4 | 85.3 |
| NW2 | 0.03 | 0.08 | 0.04 | 0.00 | 0.12 | 0.12 | 0.00 | 0.21 | 30.7 | 59.1 |
| NW3 | 0.03 | 0.07 | 0.23 | 0.01 | 0.31 | 0.85 | 0.01 | 0.94 | 75.4 | 91.0 |
| Mean TU | 0.02 | 0.06 | 0.34 | 0.00 | 0.41 | 1.23 | 0.01 | 1.31 | 74.0 | 87.3 |

BRL below the reporting limit

The map of sampling sites is shown in Fig. 1

^a TUs were calculated based on the LC50 of individual contaminant using Eq. 1. The LC50 values are listed in Table S3 in the SM. Chlorpyrifos, parathion-methyl, and terbufos were detected with concentrations greater than the reporting limits, but terbufos was not used for TU calculations due to unavailability of the LC50

^b TUs for PAHs were calculated based on the ESBs for each PAH using Eq. 1, and the ESBs are listed in Table S4 in the SM

^c TUs for PAHs were calculated using the TEC based on the sum concentrations of total PAHs, and the TEC value was 290 $\mu\text{g/g}$ OC (Swartz 1999)

Concentrations of pyrethroids in the sediments in the rural industrial area were also consistently greater than those from other functional zones. The rapid development of industry resulted in a large demand for migrant workers and increased the population. As reported, the number of migrant workers in this rural industrial area reached 13,231 persons in 2011, and it was comparable with the total population of local residents of 14,742 persons (<http://xinzaopanyu.gov.cn/SortHtml/1/318226409.html>). Due to the unbalanced development, so-called “urban villages” have appeared in this area. Urban villages are typically inhabited by poor and transient migrants, and their living conditions are overcrowded with poor sanitation (Li et al. 2013a). Pyrethroids are frequently used in professional and home pest control and landscaping maintenance in urban areas. Consequently, a correlation of pyrethroid residues and

urbanization has been noted, i.e., sediment concentrations of pyrethroids in more populous and urbanized areas were greater than those from the less developed areas (Gilliom 2007; Li et al. 2011). Although the population density in the rural industrial area (2,020 persons km^{-2} , [<http://xinzaopanyu.gov.cn/SortHtml/1/318226409.html>]) was similar to that in College City (1,902 persons km^{-2} [http://www.stats.gov.cn/tjgb/rkpcgb/dfkpcgb/t20060320_402311911.htm]), poor sanitation conditions in urban villages in the rural industrial area promoted the breeding of mosquitoes and subsequent greater demands for insecticides. Sediment concentrations of cypermethrin were comparable in the rural industrial area and other functional zones, but more permethrin residues were detected in the rural industrial area. Permethrin is primarily used for residential and professional insect control, food crops, and

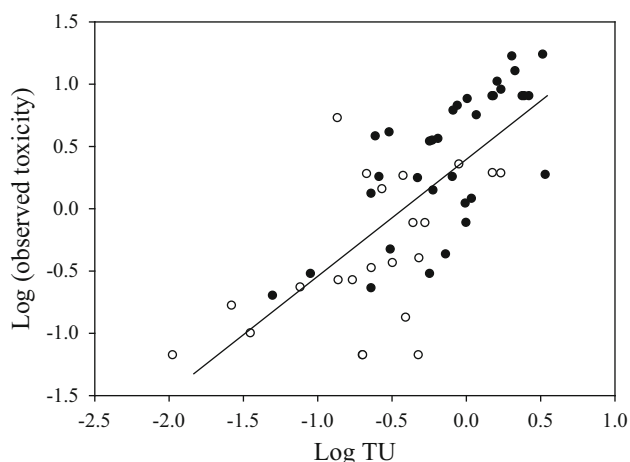


Fig. 4 Relationship between TU of pyrethroids and observed toxicity for *C. dilutus* (observed toxicity = $0.93 \text{ TU} + 0.41$, $r^2 = 0.53$, $p < 0.01$). Black circles represent data from previous studies in the PRD (Li et al. 2013a; Mehler et al. 2011), and open circles represent the data from the current study. The observed toxicity was calculated from the following equation—Observed Toxicity = $\frac{\text{Percent mortality}}{50} \times \text{dilution factor}$ —as suggested by Mehler et al. (2011). If a sediment caused 100 % mortality to the test organisms, the sediment was diluted using control sediment on a dry-weight basis for a more accurate assessment of toxicity. Therefore, the dilution factor indicated how many times the tested sediments were diluted with control sediment, with a value of 1 used for undiluted sediments

mosquito-abatement programs (USEPA 2007), which is in line with the needs of insecticides in urban villages. Therefore, the unbalanced development of urban villages in the rural industrial area may be the reason for the greater pyrethroid concentrations in this area compared with other functional zones.

Although sediments from the rural industrial areas exhibited significant greater toxicity to benthic organisms than sediments from College City, suburban villages, and Yingzhou Ecological Park, the TU values of pyrethroids were not significantly different among the four functional zones, thus implying that additional contaminants might play a role in the significantly different sediment toxicity. To identify possible toxicity contributors, Mehler et al. (2011) screened a suit of contaminants of concern, including pesticides (pyrethroids, OP pesticides, and OC pesticides), PAHs, polychlorinated biphenyls, polybrominated diphenyl ethers, metals, and ammonia and eventually concluded that pyrethroids were the principal toxicity contributors to *C. dilutus* in urban waterway sediments in the PRD. Schäfer et al. (2013) suggested that it was sufficient to estimate toxicity by solely considering the compounds with the greatest toxicity but ignoring mixture toxicity in the predominantly agricultural regions. Nevertheless, in this mixed area with various functional zones, it was difficult to identify the major toxicity contributors by simply screening a limited list of contaminants of concern.

Therefore, it is desirable in the future to perform toxicity identification evaluation to more accurately classify the toxicity contributors in College City and its adjacent areas where unbalanced economic development has caused various levels of aquatic toxicity.

In addition, most of the sediments in the current study were more toxic to *C. dilutus* than to *H. azteca* on average (Fig. 2), but this difference was significant only for the sediments in the rural industrial area. Some contaminants released from rural industrial activities may cause the significant difference in toxicity to *C. dilutus* and *H. azteca* due to their different susceptibility. For example, abamectin and fipronil were approximately 10 times more toxic than cypermethrin to *C. dilutus* but much less toxic to *H. azteca* (Ding et al. 2011). As current-use pesticides, such as abamectin and fipronil, have been widely applied in the PRD and were main toxicity contributors to *C. dilutus* in urban stream sediments in Guangzhou (Li et al. 2013a). Hence, assessing other unknown contaminants in rural industrial areas that contributed to sediment toxicity is desirable to provide more comprehensive risk assessment. In addition, toxicity to more species could be assessed in this area. By analyzing species sensitivity distribution, the information gained in the current study might be incorporated into the evaluation of overall ecosystem health in the study area.

Conclusion

Guangzhou College City and its adjacent areas were chosen as an example to evaluate the impacts of planned and unplanned developmental processes on local aquatic systems. Eight and 1 of 21 sediments exhibited acute toxicity to *C. dilutus* and *H. azteca*, respectively, with 9.5 % of the samples causing 100 % mortality to *C. dilutus*. The sediments with greater toxicity were mainly collected from the rural industrial area located in the south of College City.

Concentrations of pyrethroids in sediment in the rural industrial area were greater than those in sediments collected from other functional zones due to the greater insecticide use in this more populous and poorly sanitized area. Pyrethroids dominated the toxicity contributions among the contaminants analyzed in the current study, but the TUs of pyrethroids were not significantly different among the functional zones, suggesting that additional contaminants other than pyrethroids may play a role in the greater sediment toxicity in the rural industrial area compared with other functional zones. A significant difference in sediment toxicity to *C. dilutus* and *H. azteca* in the rural industrial area also implied the existence of other toxicity contributors. The results of our study highlight the importance of performing toxicity identification evaluation for

unknown toxicity contributors that were not on the list of contaminants of concern, especially in complex areas under unbalanced development. Although this study was performed in Guangzhou, China, this is not a local problem exclusive to China: All developing countries would benefit from more carefully planned urban development to safeguard the ecosystem.

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