Occurrence and Fate of Selected Endocrine-Disrupting Chemicals in Water and Sediment from an Urban Lake

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Abstract Occurrence of five endocrine-disrupting chemicals (EDCs)—bisphenol-A (BPA), triclosan (TCS), 17α-ethinyl estradiol (EE2), benzophenone-3, and 4-methylbenzylidene camphor—were monitored in East Lake, the largest urban lake in China. Other than EE2, all selected EDCs were detected at least once in the lake water with concentrations ≤89.1 ng/L. EDCs were detected with greater occurrence in spring than in other seasons. In lake sediment, TCS was detected at the greatest concentration (30.9 ng g^{-1}), whereas BPA and EE2 were not detected. Spatial distribution of the EDCs in the lake water and the lake sediment showed similar patterns, and greater EDC residuals were found from those sites with known wastewater input. The linear adsorption coefficients (K_d) varied from 17.9 to 1,017 L kg^{-1} and were related to the octanol–water partition coefficient (K_{ow}) values of the compounds. Photodegradation was a major process removing the EDCs from the lake water, and the presence of dissolved organic material and NO_3^- in the lake water can accelerate the photodegradation process. Degradation of the EDCs in the lake sediment was relatively slow and occurred mainly due to the microbial processes. All compounds were found more persistent under anoxic conditions than under oxic conditions.

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Endocrine-disrupting chemicals (EDCs), which can interfere with the body's endocrine system, are receiving growing concerns due to their potential to cause adverse developmental, reproductive, neurological, and immune effects to both humans and wildlife (Anway et al. 2005; Davey et al. 2007; Falconer et al. 2006). A variety of chemicals, such as certain pesticides, herbicides, surfactants, plasticizers, flame retardants, and pharmaceuticals, can potentially act as EDCs. Those chemicals are commonly used in household and industrial products and can enter the environment through municipal and industrial wastewater discharges, agricultural runoff, solid-waste leaching, and garbage incineration (Campbell et al. 2006; Kawagoshi et al. 2003; Sidhu et al. 2005). The occurrence of EDCs in the environment has been reported worldwide (Gong et al. 2009; Mayer et al. 2007; Pojana et al. 2007; Yoon et al. 2010), and increasing evidences have suggested possible adverse effects of EDCs to aquatic organisms even at environmentally relevant concentrations (Bahamonde et al. 2014; Vajda et al. 2011; Woodling et al. 2006).

The fate and behavior of EDCs in wastewater-treatment plants (WWTPs) were extensively studied because wastewater treatment is an important process preventing EDCs as well as many other pollutants from entering the environment. Tan et al. (2007) studied the removal of 15 EDCs (hormones, alkylphenols, and phthalate esters) in WWTPs using conventional activated sludge or biological nutrient removal processes from Australia and found the removal efficiency of EDCs ranged from 80 to >99 %, whereas low concentrations of EDCs can still be detected in WWTP effluent. Nakada et al. (2007) investigated the removal of phenolic EDCs and natural estrogens and found that ozonation contributed substantially to overall removal and that a combination of ozonation and sand filtration with activated sludge treatment can remove >80 % of all target

compounds. Although these studies suggested that EDCs can be removed efficiently from wastewater using current wastewater-treatment techniques, other data showed that the EDC removal was quite variable. Parameters such as temperature, hydraulic retention time, sludge age, and nitrification environment can have a pronounced effect on EDC removal (Liu et al. 2009).

Urban lakes are natural and man-made water bodies situated in urban areas. They tend to be shallow and small, are managed for direct human use, and are under intensive anthropogenic impact. Therefore, urban lakes are more vulnerable and sensitive to pollution than other water bodies. Surface runoff and both treated and untreated wastewater input from cities can introduce considerable amount of pollutants into urban lakes. Excess loads of nutrients have caused eutrophication in most urban lakes (Birch and McCaskie 1999; Jin et al. 2005). Other pollutants—such as persistent organic pollutants (Ge et al. 2014; Wang et al. 2002), heavy metals (Mahler et al. 2006), and phthalate esters (Zeng et al. 2008)—were also detected at increased concentrations in urban lakes. For protection and remediation purpose, it is important to understand the occurrence and fate of environmental pollutants in urban lake systems.

East Lake (30°33′ N, 114°23′ E), located in the city of Wuhan, is the largest urban lake in China. The surface area of the lake is 33 km[2,] and the average water depth is 2.5 m. The lake was intentionally separated into several small lakelets by bridges and dykes for public transportation, and the lakelets were connected with watercourses. More than 100 small enterprises, 11 hospitals, and 200,000 residential homes are situated around the lake (Wang et al. 2002). The lake has experienced increasing eutrophication since the mid-1970s as a result of municipal wastewater discharge. As a typical urban lake, many researches were previously performed to study the lake pollutions (Ge et al. 2014; Wang et al. 2002; Yang et al. 2007, 1998). However, limited information is available on the occurrence and fate of EDCs in the lake. Therefore, the objective of this work was to characterize the spatial distribution and seasonal variation of selected EDCs in East Lake and to investigate their adsorption and degradation behavior in the lake water and sediment.

Bisphenol-A (BPA), triclosan (TCS), 17α-ethinyl estradiol (EE2), benzophenone-3 (BP3), and 4-methylbenzylidene camphor (4-MBC) were selected as target EDCs for the investigation (Table 1). BPA is widely used in the production of polycarbonate plastics and epoxy and is present in many plastic bottles and food and beverage containers. TCS is an antibacterial agent commonly found in soaps, detergents, toothpaste, and toys. EE2 is a synthetic estrogen used in contraceptive pills for birth control. BP3 and 4-MBC are ultraviolet (UV) filters used in many

sunscreen products. All of these compounds show estrogenic activities and have been found to be widely present in the environment (Caliman and Gavrilescu 2009; Witorsch and Thomas 2010).
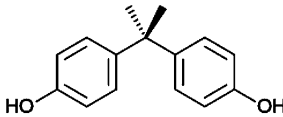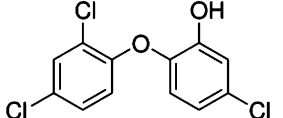
Materials and Methods
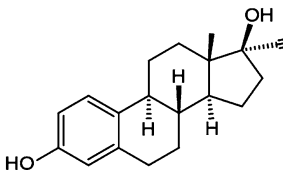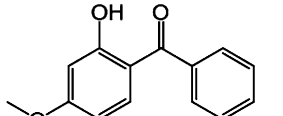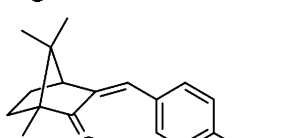
Chemicals and Standards

The standards of BPA and EE2 were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The standards of TCS, BP3, and 4-MBC were purchased from Alfa Aesar (Ward Hill, Massachusetts, USA). Internal standards of BPA-D16 and TCS-D3 were obtained from Cambridge Isotope Laboratories (Tewksbury, Massachusetts, USA). Solvents were high-performance liquid chromatography (HPLC) grade and were obtained from Tedia (Fairfield, Ohio, USA). Other chemicals were from Sigma-Aldrich (Shanghai, China). Deionized water (DI water; 18.2 MΩ-cm) was provided by a Sartorius arium basic water-purification system (Gottingen, Germany). All standards were prepared in methanol at 100 mg L^{-1} and diluted to the desired concentrations before use.

Field Investigation

Surface water (0–50 cm) samples were collected seasonally from April 2013 to January 2014 from 15 sites covering all major lakelets (Fig. 1). Surface sediment (0–20 cm) samples were only collected once in July 2013 using a grab sampler from the same sites as water sampling. Water temperature, pH, dissolved oxygen, and electric conductivity were measured in situ with a Mettler (Columbus, Ohio, USA) SevenGo Duo meter. Water samples were stored in amber glass bottles, and sediment samples were sealed in polyethylene bags. All of the samples were transported back to the laboratory in a cooler. Water samples were filtered with Whatman GF/F filters and stored at 4 °C. Sediment samples were freeze-dried and stored at −20 °C.

Water samples were extracted using solid-phase extraction (SPE) within 24 h. An aliquot of 500 mL of water sample was transferred into a beaker; 50 ng of each internal standard was added; and the sample was adjusted to pH 5. Samples were then passed through Phenomenex (Torrance, California, USA) Strata-X SPE cartridges (6 mL, 200 mg) conditioned with 2 × 3 mL DI water and 2 × 3 mL methanol at a flow rate of 5 to 10 mL min^{-1}. After loading, cartridges were vacuum-dried for 10 min and were eluated with 2 × 3 mL methanol into 10 mL glass tubes, and the eluate was reduced to 1 mL under a gentle nitrogen stream. Sediment samples were extracted

Table 1 Selected physicochemical properties of the studied EDCs

Compounds (CAS number)	Structure	Vapor pressure[a] (Pa, 25 °C)	Log K_{ow}[a]	pK_a
BPA (80-05-7)		3.03×10^{-5}	3.32	10.3[b]
TSC (3380-34-5)		6.2×10^{-5}	4.76	7.9[c]
EE2 (57-63-6)		2.6×10^{-7}	3.67	10.7[b]
BP-3 (131-57-7)		8.83×10^{-4}	3.79	7.6[d]
4-MPC (36861-47-9)		1.36×10^{-4}	5.92	–

[a] Vapor pressure and log K_{ow} are from USEPA EPI Suite software (Version 4.1)

[b] Clara et al. (2004)

[c] Loftsson et al. (2005)

[d] Rosal et al. (2010)
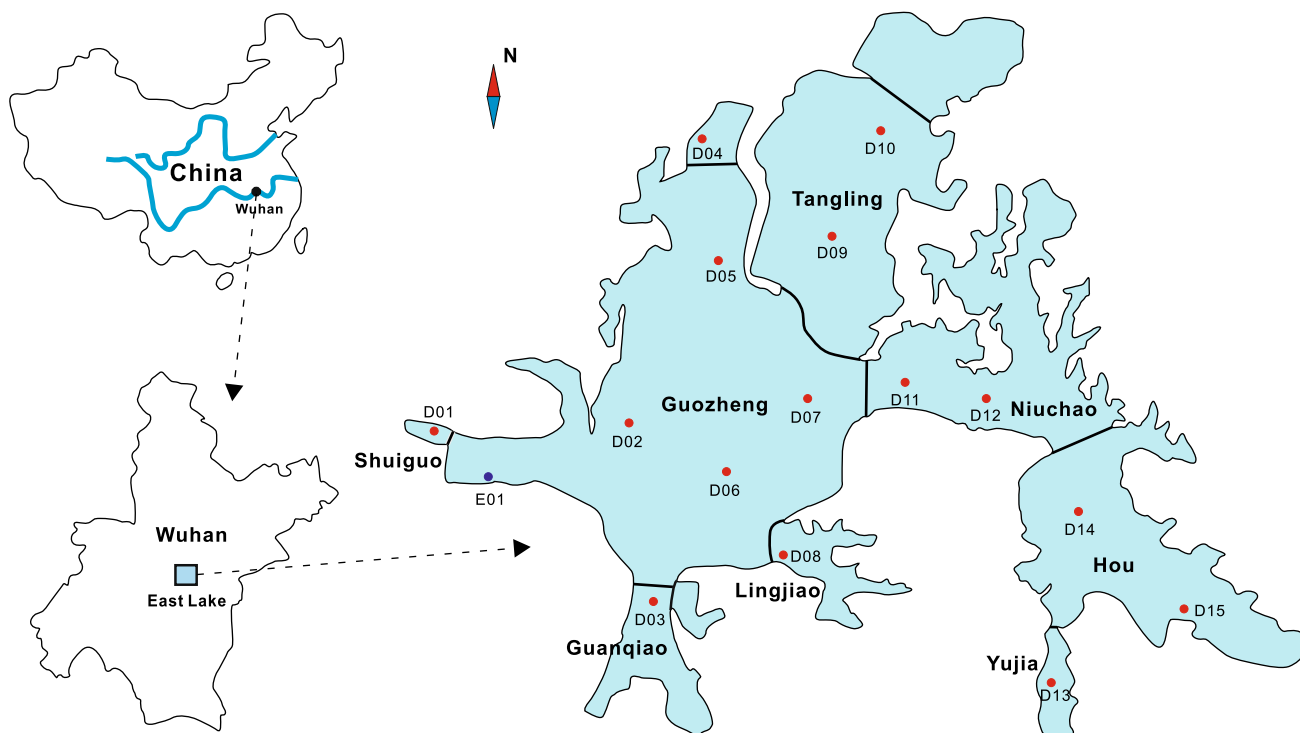
Fig. 1 Geographic location of East Lake and sampling sites in the lake

by ultrasonication. An aliquot of 5.0 g of freeze-dried sediment was transferred into a 50-mL Teflon centrifuge tube; 50 ng of each internal standard was added; and the resulting supernatant was extracted three times for 15 min with 5 mL of acetone. The extracts were collected and condensed to 1 mL under a gentle nitrogen stream. Prepared samples were transferred to 2-mL amber glass vials and stored at −20 °C until analysis.

Instrumental Analysis

Prepared samples were analyzed using a Thermo Scientific Q Exactive mass spectrometer connected with an ultra high-performance liquid chromatograph (Waltham, Massachusetts, USA). Chromatographic separation was performed on a 50 × 2.1 mm × 1.9 μm Hypersil Gold C18 column (Waltham, Massachusetts, USA). Mobile phase A was 0.5 % ammonia acetate, and mobile phase B was methanol; the total flow rate was 0.2 mL min^{-1}. The gradient started with 40 % B, ramped to 90 % in 8 min, kept for 4 min, returned to 40 % B in 2 min, and held for 5 min for equilibrium. The instrument was operated in scan mode with a mass scan range of 50–750 m/z at a resolution of 70,000. Protonated ions were used for the identification of BP3 (m/z 229.0859) and 4-MBC (m/z 255.1743). Deprotonated ions were used for the identification of BPA (m/z 227.1072), EE2 (m/z 295.1698), and TCS (m/z 286.9433). The accuracy of the method were evaluated by analyzing spiked water or sediment samples in triplicate. Recoveries and SDs of the EDCs were from 81 to 106 % and from 5 to 18 % for spiked lake water samples, and were from 85 to 93 % and from 7 to 21 % for spiked sediment samples. The method detection limit for each EDC was estimated as the lowest concentration in samples with a signal-to-noise ratio of 3, and ranged from 0.15 to 1.30 ng L^{-1} for water samples and from 0.015 to 0.13 ng g^{-1} for sediment samples. Method blank (DI water concentrated by SPE) and replicated samples were routinely analyzed for quality control. No target compound was detected in the method blank. The variation of the replicates was <23 %.

Adsorption to Sediment

Adsorption of selected EDCs onto the lake sediment was performed in triplicate using a batch equilibrium method by reference to the Organization for Economic Co-operation and Development Test Guidelines 106 (2002). Sediment sample collected from site (D11) was used for the experiment. The pH and cation exchange capacity of the sediment sample were 7.4 and 10.43 cmol kg^{-1}, and the total organic carbon (TOC), clay, silt, and sand fractions were 4.09, 60.5, 36.9, and 2.6 %, respectively. An aliquot of 0.5 g of freeze-dried sediment sample was added to a

50-mL Teflon tube filled with 40 mL of 0.01 M CaCl$_2$, and NaN$_3$ was added to a concentration of 0.01 % (w v^{-1}) to inhibit microbial activity. Prepared tubes were equilibrated by shaking on a reciprocal shaker at 200 rpm for 36 h at 25 °C in the dark. Then 80 μL of standard solution was added into each tube to achieve concentrations of 0.125, 0.25, 0.5, 0.75, 1.0, 1.5, 2.0, and 3.0 mg L^{-1}, respectively. Then the tubes were shaken for another 36 h for equilibrium. A preliminary experiment indicated that 36 h was sufficient for TCS to reach adsorption equilibrium. After equilibration, the tubes were centrifuged at 4000 rpm for 20 min, and 1 mL of the supernatant was collected for the analysis of the EDCs. The amount of EDCs in sediment was calculated as the difference between the added EDCs and the dissolved EDCs in water. The background residuals of EDCs were ignored because the background residuals accounted for <0.1 % of the added EDCs.

Concentrations of EDCs were analyzed using a Waters (Milford, Massachusetts, USA) 2,695 high-performance liquid chromatograph (HPLC) with a 2,996 photo-diode array detector (DAD). A Phenomenex Luna C8 column (100 × 4.6 mm × 3 μm) was used for the separation. Mobile phase A was acetonitrile, and mobile phase B was 0.05 % trifluoroacetic acid in DI water. The flow rate was 0.8 mL min^{-1}. The gradient started with 20 % A, hold for 2 min, ramped to 60 % in 4 min, then ramped to 80 % in 6 min, held for 8 min, then returned to 20 % in 1 min, and held for 3 min for equilibrium. The wavelengths used for the quantification of BPA, TCS, EE2, BP3, and 4-MBC were 226, 212, 212, 286, and 298 nm, respectively.

Degradation in Water

Biodegradation and hydrolysis were performed in triplicate in the dark at 25 ± 1 °C for 28 days. Water sample collected from site E01 was filtered through a paper filter (pore size 3 to 5 μm) and used in the experiment. The pH and conductivity of the water sample were 7.6 and 337 μS cm^{-1}, respectively, and the concentrations of NH$_4^+$, NO$_3^-$, and dissolved organic carbon were 0.27, 0.08, and 5.66 mg L^{-1}, respectively. An aliquot of 100 mL of lake water sample was added into a 250-mL Erlenmeyer flask. Half of the flasks were sterilized in an autoclave at 120 °C for 30 min to test the hydrolysis. All flasks were spiked with EDC standards at 2 mg L^{-1}. All flasks were then covered with breathable membranes, wrapped with aluminum foil, and incubated in a rotary shaker at 30 rpm. At specified time intervals (0, 1, 2 6, 10, 15, 21, and 28 days), 1 mL of water sample was withdrawn from each flask for the analysis of the EDCs using HPLC–DAD.

Photodegradation by sunlight was studied in August on the rooftop of the Laboratory Building of the Institute of

Hydrobiology, Chinese Academy of Sciences (Wuhan: 30.58°N, 114.28°E) according to United States Environmental Protection Agency (USEPA) guideline OPPTS 835.2210 (USEPA 1998). A standard p-nitroacetophenone–pyridine actinometer was used to measure the intensity of incident sunlight on the samples during the experiments (Dulin and Mill 1982). Quartz tubes with stoppers (diameter 20 mm, length 150 mm) were used as test vessels. Each tube was filled with 30 mL of (1) sterilized lake water (from site E01 and filtered through a GF/C filter) or (2) DI water and spiked at 2 mg/L with each EDC standard. The exposure was performed on consecutive sunny days started at noon (12:00 PM). At specified time intervals (0, 6, 24, 48, 72, and 96 h), 1 mL of sample was withdrawn from each tube for the analysis of the EDCs using HPLC–DAD. The absorption spectrum of selected EDCs was measured with a Shimadzu UV-2550 UV/visible spectrometer (Kyoto, Japan) in the range of 297.5–800 nm. All treatments were performed in triplicate.

Degradation in Sediment

Degradation of selected EDCs under oxic and anoxic conditions was studied at 25 ± 1 °C for 42 days using a similar setup as described by Jiang et al. (2010). Briefly, an aliquot of 10.0 g of wet sediment (2.4 g dry weight) was added to an amber glass vial (diameter 16 mm, length 100 mm), and 15 mL of the lake water (from site E01) was then added to the vial. One third of the vials were sterilized twice in an autoclave at 120 °C for 30 min. Then EDC standards were added to all vials to a concentration of 2 mg kg^{-1} assuming that all compounds adsorb to the sediment. Spiked sediment samples were thoroughly mixed by inverting the vials several times. All vials were stored in the dark. For oxic treatment, vials were aerated for 30 min every other day. For anoxic treatment, vials were kept airtight with caps with Teflon-lined silicone septa. For sterilized treatment, vials were covered with aluminum foil. At specified time interval, three vials were withdrawn for each treatment. Sediment samples were freeze-dried, and an aliquot of 1.0 g of sediment sample was extracted by ultrasonication as previously described. The extracts were condensed to 1 mL under a gentle nitrogen stream and analyzed using HPLC–DAD. All treatments were performed in triplicate.

Results and Discussion

EDCs in Lake Water

Concentrations of the selected EDCs in the surface water from East Lake are listed in Table 2. All target compounds were detected except EE2. 4-MBC was frequently detected in all seasons, whereas BPA was only detected in spring and summer from few sites. 4-MBC was detected at the highest concentration, which was 89.1 ng L^{-1} (spring). The average concentrations of the EDCs detected in the lake water samples varied from not detected (ND) to 14.4 ng g^{-1}. Comparing our results with data from other surface water literature, the occurrence levels of the EDCs in East Lake were at the lower end. In the Aisonas River (Greece), BPA and TCS averaged 82–122 ng/L and 22–32 ng/L, respectively (Stasinakis et al. 2012). In urban riverine water of the Pearl River Delta, China, EE2 was not detected, whereas BPA levels varied from 8 to 881 ng L^{-1} and TCS levels from 35 to 1023 ng L^{-1} (Peng et al. 2008). In Lake Zurich and Hüttnersee, Switzerland, 4-MBC levels were <2 to 22 and <2–82 ng L^{-1}, respectively, whereas BP3 levels were <2–4 and 5–125 ng L^{-1}, respectively (Poiger et al. 2004). In a previous study on xenoestrogens in East Lake performed in 2005 showed that BPA was constantly detected at concentrations $\leq$472 ng L^{-1} in water, whereas EE2 was not detected in water but was detected in suspended particles and sediment (Jin et al. 2013). Comparing our results with data from other surface water literature as well as historical data, low EDC levels in East Lake water suggest that the loadings of the selected compounds were relatively low, which is likely due to the construction of sewage-interceptor system since 1984 and still going on, which diverted most of the municipal wastewater to WWTPs, which significantly decreases the amount of wastewater input to the lake.

For the majority of compounds, their average concentrations were the highest in April (spring) and the lowest in January (winter). This is probably due to a lower consumption rate of household products containing those EDCs in winter time. Study on the occurrence of UV filters in WWTPs showed that the concentrations of the UV filters in the WW influent were greater in the hot season (July and September) than in the cool season (February) (Li et al. 2007). In winter, fewer sunscreen products are used due to a lower UV intensity. Sunscreen products are used the most in summer. However, 4-MBC from the majority of sites was found to be much greater in spring than in summer, whereas BP3 was the same range for both seasons. This might be attributed to a quicker photodegradation in summer with greater sunlight intensity. Previously, Ribeiro et al. (2009) found that BPA and EE2 were the highest in winter in the Douro River estuary, Portugal, likely due to the drought conditions. In Jiulongjiang River, South China, BPA and nonylphenol were found to be significantly greater in low-flow season (January) than in high-flow season (August), probably related to a much greater runoff volume in high-flow season causing the dilution (Zhang et al. 2012). For urban lakes, the

Table 2 Concentrations (ng L^{-1}) of the selected EDCs in surface water samples from East Lake, Wuhan, China

Site	D01	D02	D03	D04	D05	D06	D07	D08	D09	D10	D11	D12	D13	D14	D15	Mean[b]	Max	Freq[c]
April 2013 (spring)																		
BPA	9.96	ND[a]	7.49	ND	ND	ND	ND	5.27	ND	ND	ND	ND	37.1	ND	ND	3.99	37.1	4
TCS	4.47	ND	ND	ND	2.13	ND	ND	2.65	ND	ND	ND	ND	6.50	ND	ND	1.05	6.50	4
BP3	0.54	0.43	ND	0.20	3.81	ND	0.83	0.49	2.42	1.96	0.14	ND	1.53	0.15	ND	0.83	3.81	11
4-MBC	17.5	1.61	42.9	ND	25.5	ND	ND	21.3	ND	17.8	ND	ND	89.1	ND	ND	14.4	89.1	7
July 2013 (summer)																		
BPA	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.29	ND	ND	0.02	0.29	1
TCS	1.44	ND	ND	0.78	ND	ND	3.69	ND	1.55	ND	ND	ND	6.16	ND	ND	0.91	6.16	5
BP3	0.87	0.29	2.58	5.40	0.83	0.25	ND	5.99	0.21	0.86	2.80	0.29	1.70	ND	ND	1.47	5.99	12
4-MBC	3.27	0.54	5.30	1.03	1.35	2.04	ND	1.96	2.68	2.99	ND	2.09	4.53	ND	ND	1.85	5.30	11
October 2013 (autumn)																		
BPA	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0
TCS	4.99	ND	0.31	0.43	ND	0.53	0.42	ND	0.31	0.29	ND	0.65	0.77	0.32	0.82	0.66	4.99	11
BP3	ND	0.80	1.52	ND	ND	ND	ND	ND	1.25	ND	ND	ND	ND	ND	ND	0.24	1.52	3
4-MBC	ND	3.01	6.49	ND	ND	ND	3.01	0.89	5.15	2.75	1.73	3.56	4.28	ND	3.68	2.30	6.49	10
January 2014 (winter)																		
BPA	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0
TCS	0.31	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	3.26	ND	ND	0.24	3.26	2
BP3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0
4-MBC	0.47	0.59	2.96	0.72	ND	0.30	ND	1.80	ND	0.30	0.97	0.69	3.00	ND	1.35	0.88	3.00	11

[a] Not detected

[b] Zero value was used for the calculation of the mean for undetected samples

[c] Number of detected samples

fluctuation of water levels are less pronounced as a result of artificial regulation for human use. Therefore, seasonal variations in temperature, sunlight intensity, and EDC loading can be more important factors affecting the seasonal patterns of EDCs in urban lake water.

Spatial distributions of the EDCs in the lake water are presented in Fig. 2. EDCs were detected at relatively greater levels from sites D01, D03, D08, and D13, which are from the Shuiguo, Guanqiao, Lingjiao, and Yujia lakelets, respectively. For Shuiguo, Guangqiao, and Yujia lakelets, several municipal sewage outfalls exist and discharge wastewater to these lakelets, whereas the majority of municipal sewage outfalls to other lakelets were intercepted by the city sewer system to WWTPs for the treatment. EDCs in Lingjiao lakelet are probably from hospital wastewater because East Lake Hospital is the only large enterprise around the lakelet. The smaller size of Shuiguo lakelet may also cause high EDC residuals due to it having a small lake volume and thus poor water-exchange capacity. EDCs were less frequently detected and were at relatively lower concentrations from Hou (sites D14, D15) and Niuchao (sites D11, D12) lakelets. These two lakelets are within the East Lake scenic area where it is less densely populated. Only few small villages are situated around these two lakelets. Because the selected EDCs are

primarily from human sources (BPA can come from industrial sources but was only detected from few sites in this study), their spatial-distribution patterns of EDCs might reflect the municipal wastewater input status of the lakelets.

EDCs in Lake Sediment

The concentrations of selected EDCs in surface sediment from East Lake are listed in Table 3. TCS and 4-MBC were detected most frequently with concentrations varied from ND to 30.9 ng g^{-1} and from ND to 13.9 ng g^{-1}, respectively. BP3 was only detected from three sites with concentrations ≤0.23 ng g^{-1}, whereas BPA and EE2 were not detected. The average concentrations of TCS and 4-MBC were three orders of magnitude greater in sediment than in water, suggesting that both TCS and 4-MBC can accumulate in the sediment. For the rest of EDCs, their accumulation in the lake sediment is unclear due to a low detection frequency in both water and sediment. Spatially, relatively greater concentrations of EDCs were observed in sediment samples from sites D01, D03, and D13, which corresponded to the sites with greater water EDC concentrations, indicating that EDCs in the sediment came from overlaying water due to the partition and sedimentation processes.
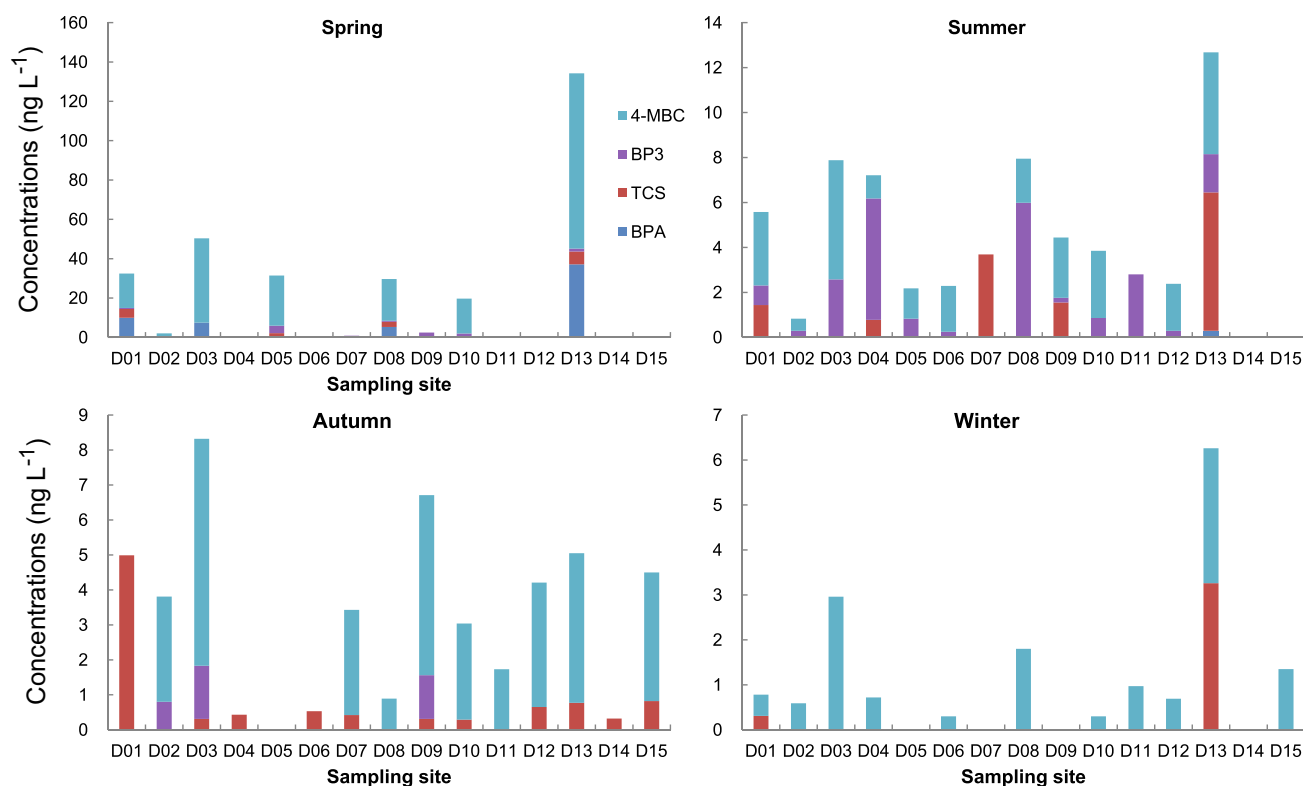
Fig. 2 Spatial distributions and seasonal variation of the EDCs in the lake water

Table 3 Concentrations (ng g^{-1}) of the selected EDCs in surface sediment samples from East Lake, Wuhan, China

Site	D01	D02	D03	D04	D05	D06	D07	D08	D09	D10	D11	D12	D13	D14	D15	Mean[a]	Max	Freq[b]
July 2013 (summer)																		
TCS	30.9	5.90	23.5	9.03	3.16	5.96	4.65	ND	1.69	1.36	1.33	0.72	11.7	1.96	1.09	7.35	30.9	14
BP3	ND	ND	0.21	ND	ND	ND	ND	ND	ND	ND	0.23	ND	0.23	ND	ND	0.04	0.23	3
4-MBC	12.0	8.66	11.10	6.69	4.64	7.54	4.87	ND	3.79	2.34	5.56	7.95	13.9	5.64	3.92	7.04	13.9	14

[a] Zero value was used for the calculation of mean for not detected samples

[b] Number of detected samples

In the Pearl River system, China, average concentrations of TCS in the sediment varied from 50.5 to 693 ng g^{-1} (Zhao et al. 2010). In sediments from Minnesota (USA) freshwater near WWTPs, TCS was detected at ≤85 ng g^{-1}, and concentrations were significantly greater from sites downstream of the WWTPs (Venkatesan et al. 2012), suggesting that effluent from WWTPs is an important source of TCS. In Japanese rivers and lakes, 4-MBC was detected neither in water nor in sediment because the use of 4-MBC as an ingredient in cosmetics is not permitted in Japan, whereas BP3 was detected with concentrations ≤164 ng L^{-1} in water but not in sediment. BP3 may have a low sorption tendency to the sediment or degrade rapidly in the sediment (Kameda et al. 2011). Comparing our results with those in the literature, selected

EDCs were also found to be relatively low, which can be attributed to their relatively low concentrations in lake water.

Adsorption of EDCs to Lake Sediment

The adsorption data are plotted in Fig. 3. The linear adsorption coefficients (K_d) between sediment and water were 17.9, 685, 40.2, 194, and 1017 L kg^{-1} for BPA, TCS, EE2, BP3, and 4-MBC, respectively. Log K_d was found to be positively related to the Log K_{ow} of the compounds ($r^2 = 0.76$), suggesting hydrophobic partition as a primary sorption mechanism. The strong adsorption capacity of TCS and 4-MBC explains the relatively high residual of these two compounds in the lake sediment. Other than
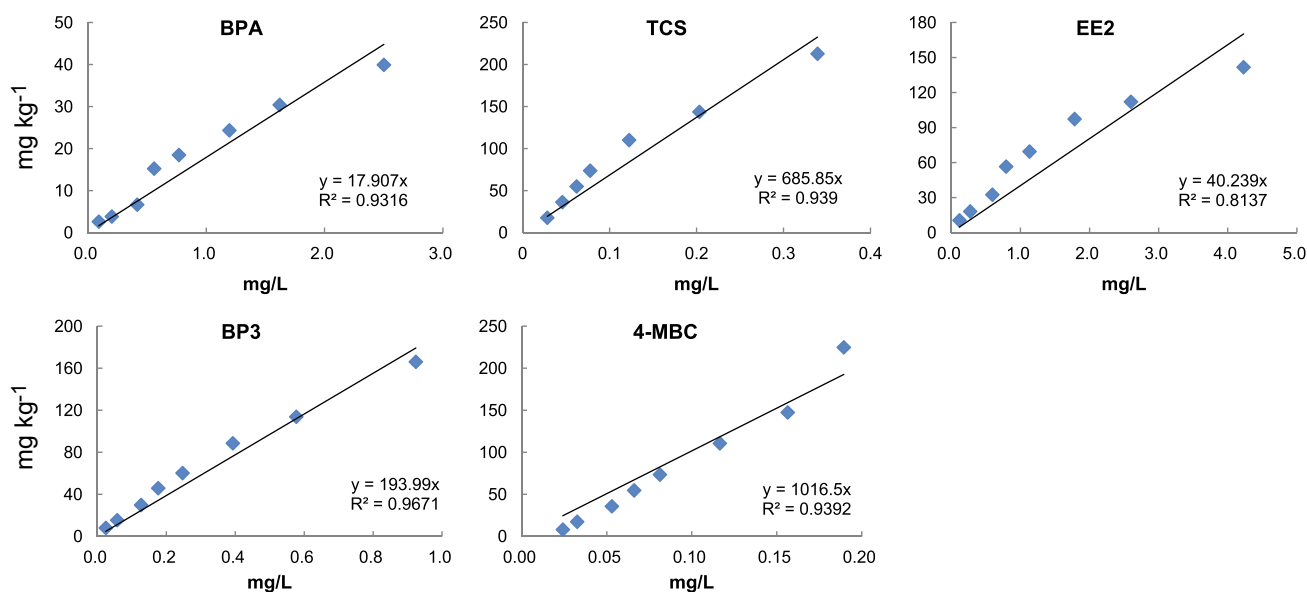
Fig. 3 Linear adsorption isotherms of the EDCs in the lake sediment

4-MBC, which is neutral, all selected EDCs were weak acids with phenol groups in their structures. Therefore, TCS ($pK_a = 7.9$) and BP3 ($pK_a = 7.6$) can partially dissociated with a sediment pH of 7.4. The sorption strength of negatively charged species in soil and sediment can be weaker than undissociated species (Chefetz et al. 2008; Wu et al. 2009). Study on the sorption of EDCs in soils from South Australia showed that K_d varied from 62 to 122 L kg^{-1} for EE2 and from 2 to 44 L/kg for BPA (Ying & Kookana 2005). The K_d values of EE2 and TCS to two loam soils were 176.2–196.8 and 256.8–282.6 L kg^{-1}, respectively (Karnjanapiboonwong et al. 2010). The results from these studies and those of our work were within the same range. Liu et al. (2013) studied the adsorption of UV filters to aquifer sediment and found that the K_d value was 1.7 L kg^{-1} for BP3 and 5.9 L kg^{-1} for 4-MBC. Their results were 2–3 orders of magnitudes lower than our results likely due to a much lower TOC content (0.4 %) of the aquifer sediment used in their experiment.

Degradation of EDCs in Lake Water

Degradation of the EDCs in both sterilized and nonsterilized lake water in the dark showed no significant [analysis of variance (ANOVA), $p > 0.3$)] decrease in concentrations over 28 days (data not shown), indicating that biodegradation and hydrolysis are of minor important for the removal of the compounds in the lake water. Photodegradation of the EDCs under sunlight is presented in Fig. 4. The photodegradation data were fitted to the first-order kinetic model. Estimated photodegradation rate constant (k_p), half-life ($t_{p1/2}$), and quantum yield (φ) are listed in

Table 4. In DI water, BPA, EE2, and BP3 showed no significant degradation in DI water (ANOVA, $p > 0.1$), whereas the concentrations of TCS and 4-MBC decreased over time with a half-life of 81.6 and 54.2 h, respectively. In lake water, the estimated $t_{p1/2}$ varied from 11.9 to 117 h. Very rapid degradation was observed for TCS, which could no longer be detected after 4 h. Our results suggest that photodegradation is an efficient pathway in removing the EDCs from the lake water. In this study, TCS showed the quickest photodegradation rate in the lake water, whereas it is still one of the most commonly detected EDCs in the environment, suggesting that TCS has a high and continuous environmental loading. In addition, photodegradation rate is related to the sunlight intensity. In winter or on cloudy days, photodegradation becomes less significant.

BPA, EE2, and BP3 cannot be photodegraded by direct sunlight exposure or the degradation process is too slow to quantify over the experimental duration. Photodegradation rates were significantly greater in the lake water than in the DI water for all of the compounds except 4-MBC, suggesting that indirect photodegradation involved in the removal of these compounds in the lake water. Quicker photodegradation in lake water can be attributed to the presence of DOM, NO_3^-, and metal ions. DOM and NO_3^- are common photosensitizers in water. DOM can promote the photodegradation by photo-inducing free radicals such as hydroxyl radicals (OH·), peroxyl radicals (ROO·), and singlet oxygen ($^1O_2$) (Chowdhury et al. 2011). NO_3^- can also produce OH· when excited by UV light at a wavelength between 290 and 330 nm (Nélieu et al. 2004).

Previously, Chin et al. (2004) found that direct photodegradation of BPA was very slow with an estimated half-
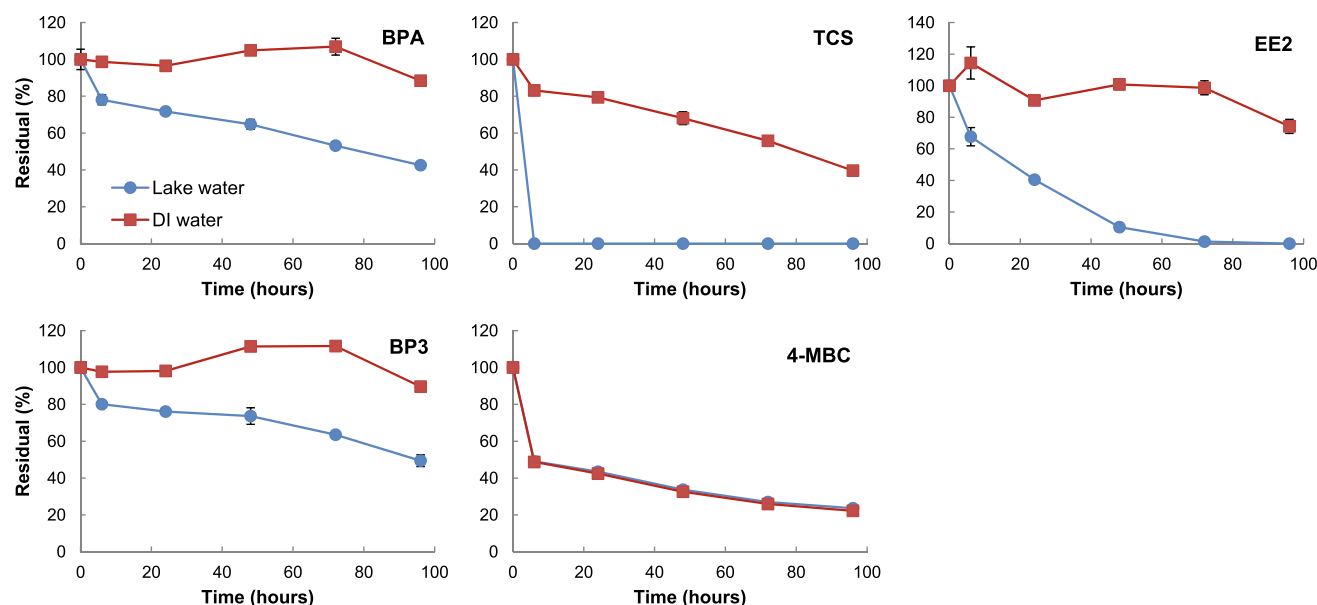
Fig. 4 Photodegradation of the EDCs in DI water and lake water samples (*error bar* represents 1 SD of triplicates)

Table 4 Photodegradation rate constant (k_p), half-life ($t_{p1/2}$), and quantum yield (φ) of the selected EDCs in the lake water under sunlight irradiation

Compound	DI water			Lake water	
	k_p (h^{-1})	$t_{p1/2}$ (h)	φ	k_p (h^{-1})	$t_{p1/2}$ (h)
BPA	NA[a]	NA	0	0.0077	90.0
TCS	0.0085	81.6	7.68E − 05	ND[b]	<4.0
EE2	NA	NA	0	0.0583	11.9
BP3	NA	NA	0	0.0059	117
4-MBC	0.0128	54.2	3.17E − 05	0.0122	56.8

[a] No significant degradation was observed (ANOVA, $p > 0.1$)

[b] No data

life of 235 h and that the presence of DOM significantly accelerated the degradation process (half-life 17.4–32.2 h). Very rapid photodegradation of TCS was also observed in wastewater irradiated with a Xenon lamp with a half-life of only 3.9 min, and 2,8-dichlorodibenzo-*p*-dioxin, which is more toxic and persistent, was identified as a major photodegradation product (Sanchez-Prado et al. 2006). These results agree with our observation. EE2 was found to be stable in bidistilled water, raw sewage, and lake water samples under UVB irradiation within 8 h (Atkinson et al. 2011). The discrepancy with our results may be due to a much shorter experimental duration used in the study. Rodil et al. (2009) studied the photodegradation of six UV filters in bidistilled water irradiated with halogen lamp (290–800 nm) and found that both BP3 and 4-MBC were stable over 72 h, but isomerization of 4-MBC was

observed. Scalia et al. (2007) studied the photostability of 4-MBC irradiated with a Xenon lamp, and the only photodegradation product exhibited the same mass spectrum as the original compound. Therefore, the observed removal of 4-MBC in this study is likely caused by photo-isomerization.

Degradation of EDCs in Lake Sediment

Degradation of EDCs in the lake sediment is presented in Fig. 5. The degradation data were fitted to the first-order kinetic model. Estimated degradation rate constant (k_b) and half-life ($t_{b1/2}$) are listed in Table 5. In the sterilized treatment, all compounds were found to be stable in the lake sediment, suggesting that abiotic processes contributed litter to the degradation of the selected EDCs. Estimated $t_{b1/2}$ for the selected EDCs varied from 3.46 to 151 days in the oxic treatment, whereas significant degradation was only observed for BPA and BP3 with an estimated $t_{b1/2}$ of 95.0 and 5.21 days, respectively. The degradation of the selected EDCs in the sediment can be mainly attributed to the microbial processes, and anoxic condition favor the persistence of the compounds. The rapid degradation of BP3 agrees with the low BP3 residuals observed in the field sediment samples.

In a previous study, TCS was found to be degraded rapidly under aerobic conditions with an estimated $t_{b1/2}$ of 18 days, whereas no degradation was observed under anaerobic conditions (Ying et al. 2007). In this study, oxic treatment was aerated every other day for 30 min. However, rapid depletion of oxygen might still occur at the
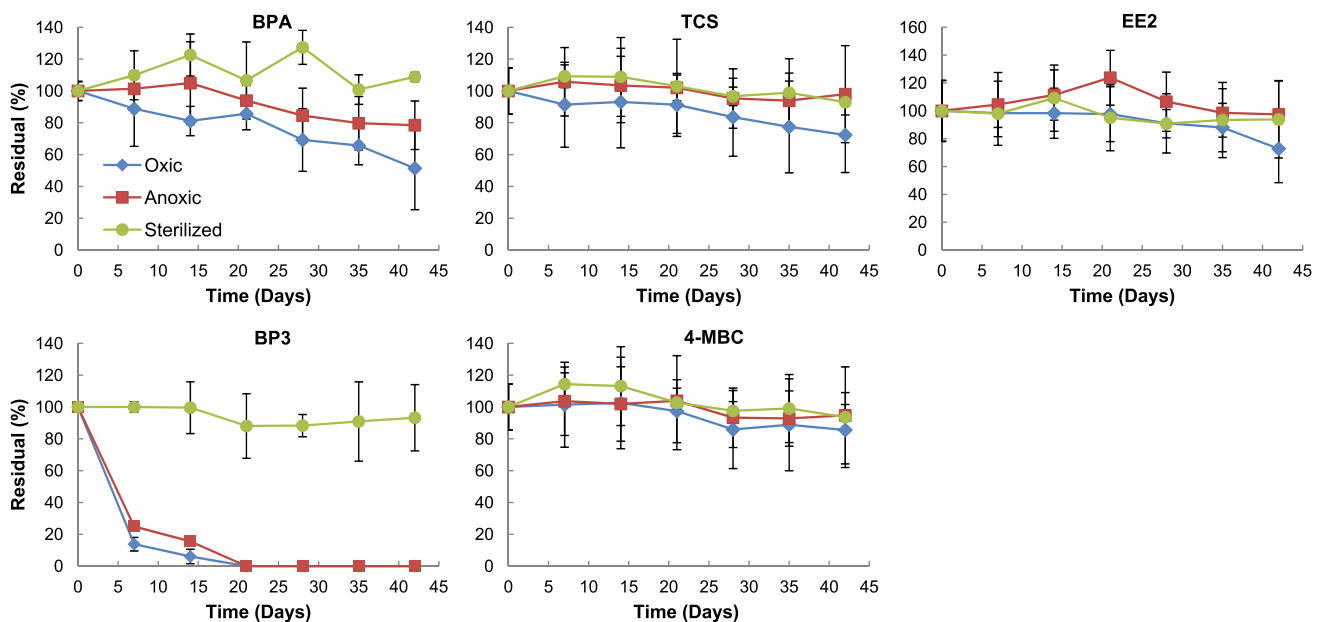
Fig. 5 Degradation of the EDCs in the sediment (*error bar* represents 1 SD of triplicates)

Table 5 Degradation rate constant (k_b) and half-life ($t_{b1/2}$) of the selected EDCs in the lake sediment

Compound	Oxic		Anoxic	
	k_b (day^{-1})	$t_{b1/2}$ (day)	k_b (day^{-1})	$t_{b1/2}$ (day)
BPA	0.0141	49.2	0.0073	95.0
TCS	0.0072	96.3	ND[a]	ND
EE2	0.0064	108	ND	ND
BP3	0.2	3.46	0.1331	5.21
4-MBC	0.0046	151	ND	ND

[a] No degradation

water–sediment interface as a result of microbial respiration. Therefore, the degradation of TCS was much slower in the sediment than in the soil. Ying et al. (2003) found that EE2 degraded in the aquifer media under aerobic conditions with an estimated $t_{b1/2}$ of 81 days, whereas BPA was stable under both aerobic and anaerobic condition. In another study, the estimated $t_{b1/2}$ values were 0.29 and 1.212 days under aerobic conditions and were 1.1 and 1.38 days, respectively, for the degradation of EE2 and BPA in river water–sediment slurries (Sarmah and North-cott 2008). Rapid degradation of BP-3 was also reported in aquifer materials with estimated $t_{b1/2}$ values of 5.3 and 1.5 days under aerobic and anaerobic conditions, respectively, which agree with our observation. However, degradation of 4-MBC was observed under both aerobic ($t_{b1/2}$ = 33 days) and anaerobic ($t_{b1/2}$ = 75 days) conditions (Liu et al. 2013), whereas 4-MBC was found to be stable according to our results. The discrepancy might be

attributed to the difference in substrate properties. The difference in TOC content may affect the sorption strength of the compounds and therefore their availability for bio-degradation. Different substrates can also have different microbial activities that affect their degradation abilities (Yang et al. 2011). Previous exposure of the substrate might also facilitate the acclimation of the microbial community and lead to a faster degradation of the target compound (Tuxen et al. 2002).

Conclusion

Selected EDCs were frequently detected in water and sediment samples from East Lake, but their concentrations were found to be relatively low compared with date in the literature, a likely benefit from the city sewage interceptor projects which begun in early 1980s. Greater occurrence of EDCs was observed in spring and was detected from sites receiving wastewater input. Adsorption experiments showed that selected EDCs had a moderate to strong affiliation to the lake sediment. Results of the degradation experiment suggested that indirect photodegradation can quickly remove EDCs from the lake water. EDCs, except BP3, were relatively stable in the lake sediment, and all of the EDCs were found to be more persistent under anoxic conditions. Field data, together with data from laboratory experiments, suggest that (1) photodegradation and partitioning to sediment are two important processes controlling the fate of EDCs in lake water and (2) degradation of EDCs in lake sediment is a slow process, and (3) anoxic

conditions, which are likely to occur in eutrophicated lakes, favor the preservation of the compounds.

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