Occurrence of endocrine-disrupting chemicals in riverine sediments from the Pearl River Delta, China

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ABSTRACT

The endocrine-disrupting chemicals (EDCs) was investigated in 28 riverine sediments from the Pearl River system, China and analyzed by an ultrasonication extraction and GC–MS method. The concentrations of 4-*tert*-octylphenol (OP), 4-nonylphenol (NP), and bisphenol A (BPA) in the sediments were in the ranges of <2.0–210, 107–16198 and <1.7–430 ng/g dw, respectively. The steroid estrogens estrone (E1) and 17β-estradiol (E2) in the sediments ranged from <1.3 to 10.9 ng/g dw and from <0.9 to 2.6 ng/g dw, respectively. The spatial distribution of these chemicals was related to the discharge of domestic and industrial wastewater along the rivers. The positive correlation between EDCs and total organic carbon indicates that sedimentary organic carbon is an important factor in controlling the distributions of EDCs. Compared with other previous studies, the ZR and DR rivers from the PRD were heavily contaminated by APs and BPA.

1. Introduction

The occurrence of endocrine-disrupting chemicals (EDCs) in aquatic environments has become a globally growing problem of concern in recent decade. EDCs consist of a wide range of natural and man-made chemicals, most of which are released to natural waters by anthropogenic activities and whose adverse effects on normal reproductive functions of aquatic species have widely been confirmed (Jobling et al., 1996; Routledge et al., 1998; Oehlmann, 2000; Irwin et al., 2001; Levy et al., 2004). For instance, widespread estrogenic chemical input has been regarded as an important factor related to the decline of fish abundance in freshwater systems (Jobling et al., 1998; Burkhardt-Holm et al., 2005; Kidd et al., 2007). Among this group of chemicals, steroid estrogens (e.g. estrone, 17β-estradiol and 17α-ethynylestradiol) and phenolic xenoestrogens (e.g. alkylphenols and bisphenol A) deserve particular attention as the former possesses the highest estrogenicity and the latter has moderately estrogenic potency and massive usage (Ying et al., 2002).

Due to their hydrophobic nature, EDCs in the river water tend to be associated with particulate matters that can be settled to bottom sediments and accumulated continuously. Therefore the sediments act both as a long-term pollutant sink and reservoir, and as a source of contaminants through re-suspension. They may also pose a potential environmental threat to aquatic organisms. Owing to the importance of sediments on the transport, fate and bioavailability of EDCs, investigations on the sediment contamination of EDCs have been widely carried out (Naylor et al., 1992; Hale et al., 2000; Isobe et al., 2001; Heemken et al., 2001; López de Alda et al., 2002; Jonkers et al., 2003; Rice et al., 2003; Li et al., 2004a,b; Patrolecco et al., 2004; Chen et al., 2006; Fu et al., 2007; Labadie et al., 2007), and phenolic xenoestrogens with high levels were reported worldwide. For example, the sedimentary concentrations of nonylphenol and octylphenol were up to 72,000 ng/g and 1800 ng/g dw, respectively, from Hamilton Harbor of the Great Lakes, Canada, which was highly impacted by anthropogenic activities (Bennie et al., 1997). Although estrogen-monitoring studies have been conducted in more than 30 countries, limited studies on the occurrence and distribution of EDCs, in particular, steroid estrogens, in riverine sediments were carried out in the developing countries including China (Gong et al., 2009), which is growing to be the world factory with the largest population in the world.

The Pearl River Delta (PRD) is one of the most economically developed regions in China, covering an area of 41700 km^2 with a population of 42.3 million. It is subjected to the typical subtropical climate featured with mild temperatures and rich annual rainfalls, facilitating the transport of contaminants to the aquatic environments through waste discharge, surface runoff and aerial fallout, etc. The limited studies indicated that the total suspended particulate matter is 445 Tg/year for the Pearl River system, and the transported particulate organic carbon is 2.93 Tg C/year and 0.30 Tg C/year in the West River and North River, respectively

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(Gao et al., 2002). Moreover, it is estimated that industrial and domestic wastewaters amount to 5.8×10^9 and 2.8×10^9 tons, respectively, annually in the PRD, but more than half of the wastewaters are not treated effectively prior to discharge. In recent three decades, the regional aquatic environment pollution is increasingly serious with the heavily industrialized and urbanized development. Furthermore, the local fishery resources declined unceasingly, and biomass and biodiversity displayed a decreasing trend in the past decade (Lin and Han, 2001). In the present investigation, eight estrogenic EDCs, that is, natural steroid estrogens including estrone (E1), 17β-estradiol (E2), and estriol (E3), synthetic steroid estrogens including 17α-ethynylestradiol (EE2) and diethylstilbestrol (DES), and phenolic xenoestrogens encompassing 4-tert-octylphenol (OP), 4-nonylphenol (NP) and bisphenol A (BPA) were determined in the surface sediments of the rivers from the PRD and the total organic carbon (TOC) contents were analyzed, aiming to provide comprehensive sedimentary concentration levels of estrogenic chemicals in rivers from the PRD, reveal their spatial distribution, explore their interaction with organic carbon, and briefly assess the present pollution status of EDCs by comparison with previous studies around the world.

2. Materials and methods

2.1. Study area description and sample collection

The Pearl River system is the second largest river in China in terms of annual discharge (3.49×10^{11} m³). It mainly comprises four tributaries, namely, the Zhujiang River (ZR), Dongjiang River (DR), Beijiang River (BR) and Xijiang River (XR), and merges into the Pearl River Estuary (Fig. 1). ZR runs across metropolitan Guangzhou, the biggest city in the south of China, which is highly urbanized with a population of 14 million. DR flows through Dongguan city which is intensely industrialized and highly populated, serving as the drinking water source of Dongguan, Shenzhen, and Hong Kong. The two rivers drain into the Shizhiyang Waterway. XR and BR lying in the southwest of the PRD run across less developed and dispersedly populated areas. 28 surface sediments (0–20 cm) were collected from these four major streams (Fig. 1) in July 2006 and February 2007, respectively, using a stainless steel grab sampler. The sediment samples were stored at −20 °C until further analysis.

2.2. Chemicals

HPLC-grade acetonitrile (Merck), ethyl acetate (Sigma), redistilled analytical grade solvents including methanol (MeOH), dichloromethane (DCM), hexane and acetone, and redistilled water were used for the analysis. Standards of 4-nonylphenol (mixture of compounds with branched side chain) (94%), 4-tert-octylphenol (93%), bisphenol A (BPA), estrone (E1), 17β-estradiol (E2), estriol (E3), 17α-ethynylestradiol (EE2) and diethylstilbestrol (DES) were purchased from Sigma–Aldrich (St. Lois, MO, USA). The derivatization reagent N-methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA) was also obtained from Sigma–Aldrich. Deuterated bisphenol A (BPA-d_{16}), estrone (E1-d_4) and 17β-estradiol (E2-d_2) were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). Deuterated terphenyl (terphenyl-d_{14}) and ENVI-18 SPE cartridges (300 mg, 3 mL) were obtained from Supelco (Bellefonte, PA, USA). Neutral silica gel (80–100 mesh) was Soxhlet extracted with DCM for 72 h, activated at 180 °C for 12 h and then deactivated by adding 5% redistilled water (w/w). Glasswares and anhydrous sodium sulfate were baked at 450 °C for 4 h prior to use.

2.3. Extraction, cleanup and derivatization

The sediments were freeze-dried under −47 °C for 24 h, and sieved through an 80-meshed stainless steel mesh. Five gram of each sample was put into a 20-mL glass vial with PTFE screw cap and spiked with BPA-d_{16}, E1-d_4 and E2-d_2 as surrogate standards, and activated copper was also added for desulfurization. The mixture was blended and soaked in 10 mL of MeOH for 2 h in dark prior to ultrasonication. The slurry of the sample was ultrasonicated for 5 min and then centrifuged at 2500 rpm for 5 min, and the supernatant was collected. The extraction was repeated twice with 10 mL of MeOH and then twice with 10 mL acetone and the four fractions were combined.

The sediment extracts were concentrated to about 1 mL using a rotary evaporator and transferred to a glass column filled with 1 g of anhydrous sodium sulfate and 1.5 g of silica gel pre-conditioned with ethyl acetate/hexane (40:60). The analytes were eluted using 20 mL of ethyl acetate/hexane (40:60), evaporated to dryness by rotary evaporation and a gentle nitrogen gas stream sequentially, and re-dissolved in 1 mL of MeOH/acetone (1:1) and then mixed with 100 mL of redistilled water. The mixture was passed through an ENVI-18 SPE cartridge pre-conditioned with 5 mL of methanol
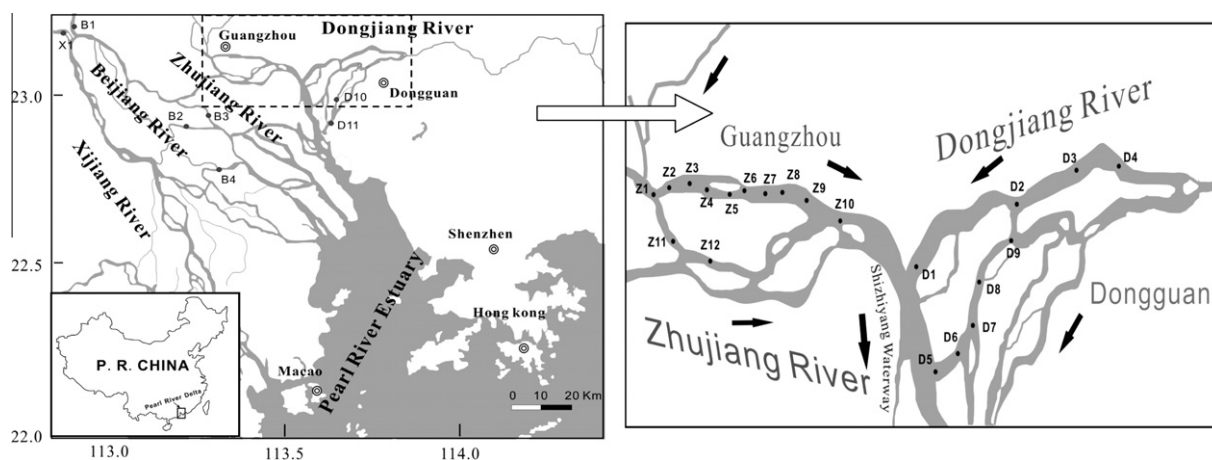

Fig. 1. The locations of sampling sites in the Pearl River Delta. The arrows in the right graph indicate the water flow direction.

and 5 mL of redistilled water sequentially at a flow rate of 8–10 mL/min. Subsequently, the analytes were eluted using 8 mL of acetonitrile after the SPE catridge was dried under vacuum pressure for 30 min. The eluate was dehydrated with anhydrous sodium sulfate and concentrated to 1 mL by rotary evaporation prior to derivatization.

The sediment extracts and calibration standards were evaporated to dryness under a gentle nitrogen gas stream, followed by addition of 50 μL of ethyl acetate and 100 μL of MSTFA, and heated in a water bath at 70 °C for 30 min and then cooled to room temperature. After derivatization each of them was spiked with terphenyl-d_{14} as the internal standard and adjusted to a final volume of 200 μL with ethyl acetate for further instrument analysis.

2.4. Quantification

Separation and detection of EDCs was achieved by a Thermo GC–MS system consisting of a TRACE GC ULTRA gas chromatograph, an AS 3000 autosampler, and a DSQ quadrupole mass spectrometer equipped with EI source. A DB-5 (J&W Scientific) fused silica capillary column (30 m × 0.25 μm × 0.25 mm i.d.) was used with helium as the carrier gas at a constant flow of 1 ml/min. The injection port, transfer line, and ion source temperatures were set at 250, 280, and 250 °C, respectively. The oven temperature was held at 50 °C for 1 min, then programmed at 20 °C min^{-1} to 200 °C, at 3 °C min^{-1} to 280 °C, at 30 °C min^{-1} to 290 °C, and held for 5 min. One microliter of the derivatized extract or standard solution was injected in splitless mode and a selected ion monitoring mode (SIM) was employed after the solvent delay for 8 min. Limits of quantification (LOQ), estimated with the ratio of signal to noise ($S/N = 3$), and quantification ion peaks (m/z) are listed in Table S1.

2.5. Qa/qc

Spiked blanks (eight EDCs standards spiked into solvents) were analyzed and the average recoveries of OP, NP, BPA, DES, E1, E2, EE2, and E3 were 85.6 ± 10.7%, 109.9 ± 5.6%, 125.8 ± 12.2%, 89.1 ± 3.3%, 98.1 ± 14.5%, 95.9 ± 7.6%, 90.3 ± 16.1% and 97.0 ± 14.3%, respectively ($n = 3$). Furthermore, surrogate standards BPA-d_{16}, E1-d_4 and E2-d_2 were added to all the sediment samples to monitor procedural performance and matrix effects, and their recoveries were 101.5 ± 9.1%, 93.1 ± 12.3% and 115.7 ± 14.8%, respectively. Procedural blanks were analyzed with the samples as well. OP was detected but the amounts were under the LOQ, and NP and BAP are on average 20 and 2.0 ng g^{-1} dry weight, respectively in the blanks ($n = 3$), and other target compounds were all not detectable. The reported data were not corrected by the surrogate recoveries but were corrected by the blank.

2.6. Analysis of organic carbon

The analytical methods for organic carbon in the sediment samples were documented elsewhere (Ran et al., 2002). In brief, about 5 g of the frozen-dried sediment sample was treated with 10% HCl for 24 h to remove inorganic carbon, and then dried overnight at 105 °C. The organic carbon contents were determined on an elemental analyzer (Vario EL III Elementar, Germany) with acetanilide used as external standard. Sample duplicates were processed and their mean values were reported with relative standard derivation less than 1%.

3. Results and discussion

3.1. Composition and distribution of EDCs in sediments of rivers from the PRD

Concentrations of selected EDCs in the surface sediments are listed in Table 1. Alkylphenols (APs) i.e. OP and NP, and BPA were detectable in all the samples, and the concentrations of OP, NP and BPA ranged from <2.0 to 210 ng/g dw (dry weight), 107 to 16198 ng/g dw and <1.7 to 430 ng/g dw, with a median of 19.1, 3071 and 65.1 ng/g dw, respectively. The natural estrogens E1 and E2 were detected in 71.4% and 64.3% of the sediment samples, respectively. E1 was determined at concentrations ranging from <1.3 to 10.9 ng/g dw with a median of 3.5 ng/g dw, while E2 was lower and in a range of <0.9–2.6 ng/g dw with a median of 1.4 ng/g dw. The other target chemicals including DES, EE2 and E3 were not detectable. Obviously the concentration of NP was 1–3 orders of magnitude higher than that of other EDCs, and the concentrations of OP and BPA were in the similar range that was 1 order of magnitude higher than those of E1 and E2. It was noted that the sedimentary NP concentrations were 1–2 order magnitude higher than those of OP (Table 1), consistent with other observations on riverine sediments in other countries (Bennie et al., 1997; Snyder et al., 1999; Ferguson et al., 2001; Blackburn et al., 1999; Tsuda et al., 2000; Isobe et al., 2001; Heemken et al., 2001). This observation demonstrated that nonylphenol ethoxylates (NPEOs), precursors of NP, dominated the usage of alkylphenol ethoxylates (APEOs), precursors of APs, in the PRD areas. In addition, a synchronous changing tendency was observed for OP and NP (Fig. S1). Their parallel fluctuation patterns were probably attributed to their similar physicochemical properties and sources.

Table 1
EDCs concentrations in surface sediments from rivers in the Pearl River Delta.

Sampling site	Concentration (ng/g dw)						
	OP	NP	BPA	E1	E2	∑APs[a]	TOC[b] (%)
Z1	35.6	4447	82.5	4.0	1.9	4483	2.3
Z2	32.7	4863	94.5	5.0	1.7	4896	3.5
Z3	27.2	3928	67.5	5.4	1.5	3955	3.6
Z4	56.9	7610	100.4	7.1	2.6	7667	4
Z5	39.5	5827	96.2	5.3	2.0	5867	3.6
Z6	19.1	2496	30.0	2.9	1.0	2515	1.6
Z7	11.2	2061	23.3	1.7	1.3	2072	1.7
Z8	40.8	6507	79.5	1.9	1.8	6548	2.1
Z9	14.4	3080	89.2	1.3	1.0	3094	1.9
Z10	12.6	2938	32.9	<LOQ[c]	nd[d]	2951	1.8
Z11	142.1	16198	274.9	10.9	3.8	16340	12.7
Z12	14.0	2635	65.1	2.5	1.2	2649	2.9
D1	30.8	7845	60.2	nd	nd	7876	2.3
D2	210.1	5107	376.2	1.6	nd	5317	7.9
D3	17.0	1453	38.1	<LOQ	<LOQ	1470	2.8
D4	3.2	289	14.3	<LOQ	0.9	292	1.6
D5	21.1	3168	44.2	nd	nd	3189	1.9
D6	31.1	4190	92.9	nd	nd	4221	2.4
D7	44.4	3786	283.9	<LOQ	nd	3830	3.3
D8	16.8	3062	100.8	<LOQ	<LOQ	3078	2.6
D9	103.1	6634	429.5	nd	nd	6737	3.8
D10	16.4	2530	17.6	<LOD	nd	2546	1.5
D11	9.3	1685	20.2	nd	nd	1695	1.3
B1	2.5	216	2.1	nd	<LOQ	219	0.4
B2	2.3	107	3.8	nd	nd	110	1
B3	<LOQ	117	4.1	<LOQ	0.9	117	1
B4	2.7	205	27.6	<LOQ	<LOQ	208	1.3
X1	2.5	118	<LOQ	nd	1.0	120	1.4
Median	19.1	3071	65.1	3.5	1.4	3086	
Mean	35.5	3682	94.5	4.1	1.6	3717	

[a] Total of OP and NP.
[b] Total organic carbon.
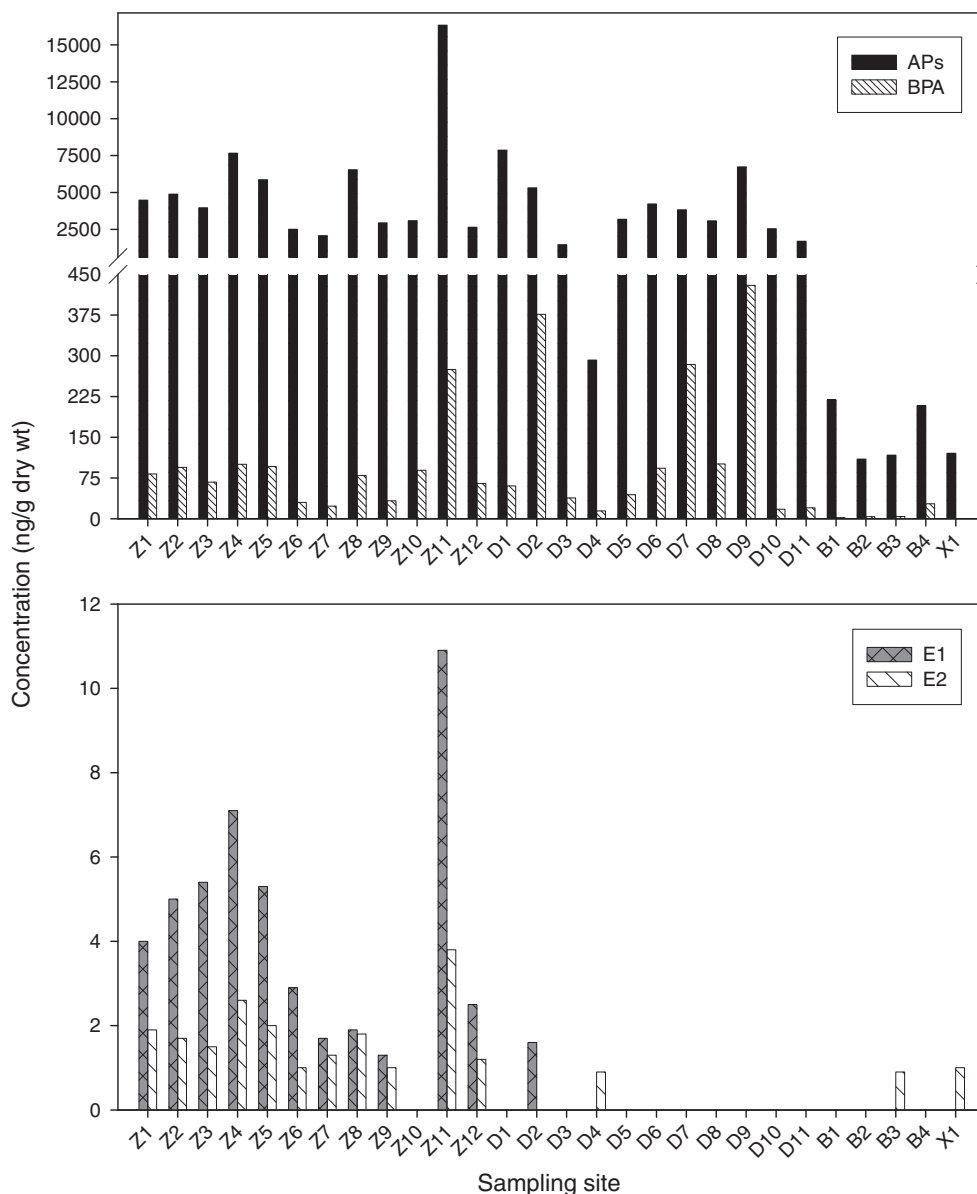[c] Limit of quantification.
[d] Not detected.

Fig. 2. Spatial distribution of EDCs in surface sediments from rivers of the Pearl River Delta.

On the whole, high value ranges of APs in the world (see below discussion) were found in the surface sediments of the rivers from the PRD, and the EDCs pollution was dominated by phenolic xenoestrogens including OP, NP and BPA, whilst natural estrogens E1 and E2 were at low levels.

The spatial distribution of the EDCs in the surface sediments of the rivers from the PRD is shown in Fig. 2. The concentrations of $\sum$APs (total of OP and NP) was evidently higher in ZR (Z1–Z12) (Fig. 1) than in the other rivers. $\sum$APs in ZR were in a range from 2072 to 16340 ng/g dw, in which the highest was found at Z11 of the back channel (Z11–Z12), while the highest one in the front channel (Z2–Z10) was found at Z4. On a whole, $\sum$APs varied indistinctively from the upstream Z1 to the downstream Z10, except for Z11 where the surface sediment could be polluted by point sources nearby. Such pollution characteristic in ZR was similar to that in Sumidagawa River, Japan (Isobe et al., 2001), with the high concentrations of $\sum$APs in the riverine sediments attributed to massive amount of wastewater discharge from the metropolitan area. Similar spatial distribution was also observed for BPA in this river, where its concentrations ranged between 23.2–274.9 ng/

g dw. The natural estrogens E1 and E2 were mainly found in ZR with detectable percents of 100% and 91% in the sediments, respectively, while they were rarely detected in the sediments of the other investigated rivers. The concentrations of E1 and E2 were in the range of <1.3–10.9 ng/g dw and nd-3.8 ng/g dw, respectively, and both of the two estrogens were primarily derived from the abusively discharged raw sewages from hundreds of watercourses of Guangzhou city (Peng et al., 2008). The distribution pattern of E1 was featured with a first increasing (Z1–Z4) and then decreasing (Z4–Z9) trend along the river, suggesting that there were new contaminant sources near the midstream running across the central area of Guangzhou city, while the pattern of E2 was analogous to those of APs and BPA. Additionally the maximum of the both estrogens were measured at Z11, while the minimum appeared at downstream Z10, far from downtown of Guangzhou, and the concentrations of E1 and E2 in the sediments of the other rivers were in a small variation. Interestingly, all of the maximum concentrations of these EDCs were found at Z11, reaffirming the presence of contamination sources near this site. Additional investigations found that a spice factory and a pharmaceutical factory were situated near

Z11 and a watercourse receiving sewage from residential districts nearby joined ZR. Therefore, the untreated wastewater and sewage discharged from these factories and residential areas can be responsible for the high levels of EDCs in the sediment sample Z11.

The concentrations of $\sum$APs (292–7876 ng/g dw) in DR (D1–D9) were slightly lower than that in ZR and much higher than those in BJ (B1–B4) and XR (X1). There was an obvious trend for the $\sum$APs concentrations increasing from the upstream to the downstream in the north major stream (D4–D1). Apart from the local contaminations, D1 was influenced by the effluent discharging from the local sewage treatment plants of Guangzhou Development Zone located at the north bank, leading to the maximum value of $\sum$APs in DR at this site. Besides, the most APs-polluted site in the south branch streams (D5–D11) was D9 situated in the middle between two highly industrialized towns Zhongtang and Wangniudun, which contributed considerable amounts of wastewater originated from local hundreds of manufacturing and processing facilities. However, $\sum$APs concentrations varied indistinctively in the south branch streams. This was probably related to horizontally mixing of the river water with the ocean water by the tidal effect, as the lower sites of these branches are near the river estuaries. BPA concentrations ranged from 14.3 to 429.5 ng/g dw in DR, and the min-

imum and maximum values were found at D4 and D9, respectively. In general, BPA levels were relatively low in the upstream sites, much higher in the midstream sites, and gradually decreased down the stream toward the estuary. Such distribution feature could be related to the industrial discharge in Dongguan, and the dilution by the large amount of water from the Shizhiyang Waterway. The E1 concentrations in most of the DR sediment samples were lower than its LOQ or undetectable, while E2 was merely detected in three of all the sediment samples.

The EDCs-contaminated level in BR and XR was the lowest with $\sum$APs and BPA ranging from 110 ng/g dw to 219 ng/g dw and from 1.7 ng/g dw to 27.6 ng/g dw, respectively, while the natural estrogens E1 and E2 were mostly under their LOQs or not detected. This could be due to the fact that BR and XR mainly pass through the rural areas of the PRD with low anthropogenic input, and both of the two rivers have massive runoff volumes, which tend to dilute the contaminant inputs along the rivers.

3.2. Correlations of EDCs with sedimentary organic carbon

Since the sedimentary organic carbon is an important factor in the sorption of EDCs (John et al., 2000; Ferguson et al., 2001), the
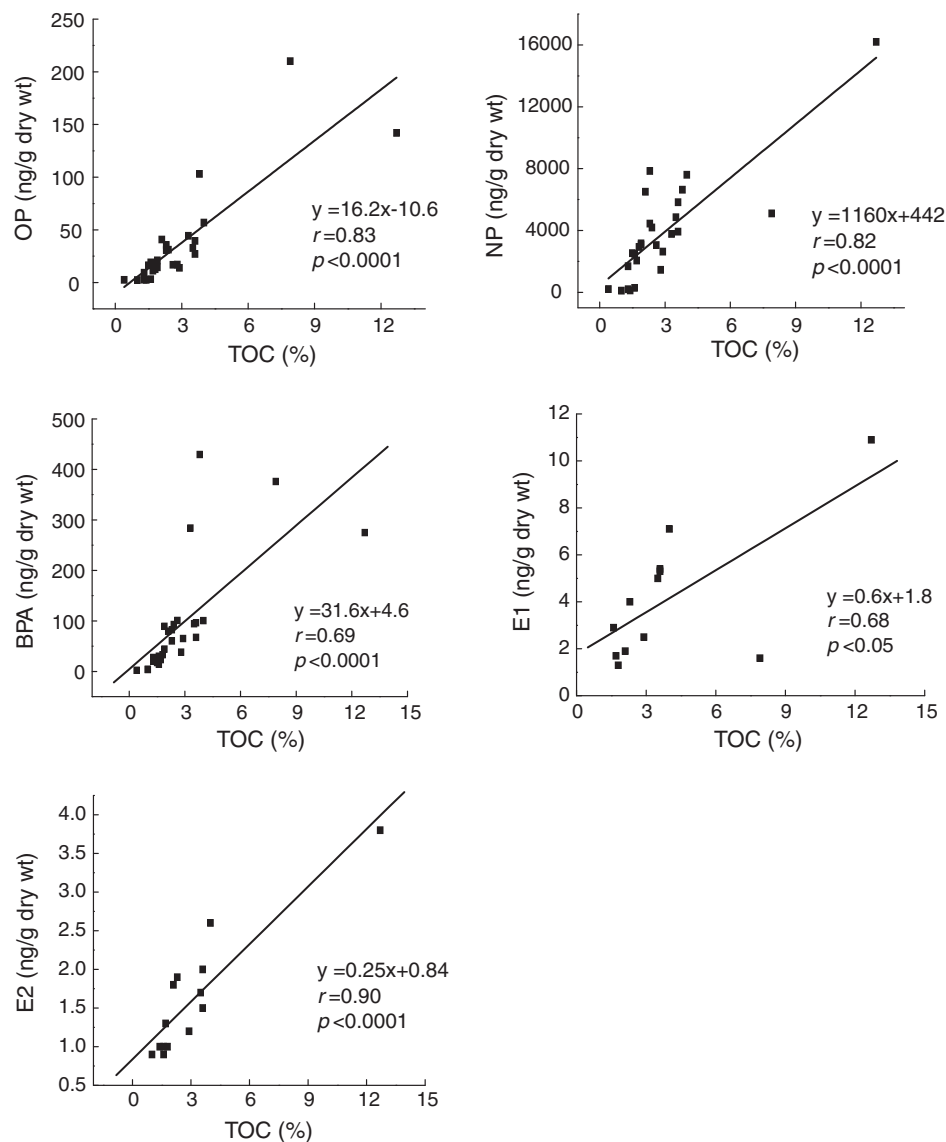

Fig. 3. Correlations between EDCs concentrations and TOC contents in the sediment samples.

influence of the total organic carbon (TOC) on the distribution of APs and other estrogens in our surface sediments was investigated using linear regression analysis conducted by the software of Origin 8. It was found that OP, NP and E2 were significantly correlated with TOC contents and their correlation coefficients (r) were 0.83, 0.82 and 0.90 (Fig. 3), respectively, suggesting that these chemicals could be mainly associated with organic-rich sediments through hydrophobic interaction, in virtue of their higher hydrophobicity with a log K_{ow} value of 4.12, 4.48 (Ahel and Giger, 1993), and 3.94 (Lai et al., 2000) for OP, NP and E2, respectively. However, moderate correlations were yielded between BPA, E1, and TOC contents ($r = 0.69$ and 0.68, respectively) (Fig. 3), which was probably related to their smaller log K_{ow} values of 3.32 (Staples et al., 1998) and 3.94 (Lai et al., 2000) for BPA and E1, respectively. Besides, other binding mechanisms to the sediment other than hydrophobic interaction with organic matters could be effective and responsible. For example, compared with OP, NP and E2, BPA and E1 can be associated with sedimentary minerals such as iron oxide by ion exchange (Lai et al., 2000) due to their relatively higher polarity. In addition, less significant correlations between BPA, E1 and TOC contents suggested that the spatial distribution of BPA and E1 was not only controlled by the TOC contents of the sediments, but also depended on other factors, such as the discharge amount of the contaminants from local point-source sites, i.e., D2 and D9 for BPA.

To sum up, the positive correlation between EDCs and TOC indicates that sedimentary organic carbon (SOC) is a key factor in controlling the distributions of EDCs. The sorption of EDCs to the sedimentary organic matters (SOM) plays a important role, which is consistent with other studies (Jonkers et al., 2003; Lai et al., 2000).

3.3. Comparison with other areas in the world

The concentrations of EDCs in the surface sediments of this investigation were compared with those of other domestic and overseas investigations, which are listed in Table 2. It was found that the APs concentrations analyzed in the present work are generally higher than those documented in a previous study on the PRD (Chen et al., 2006), indicating that the APs contamination in the rivers from the PRD is still increasing during these years. Except for the highly polluted sediments in the Donghu Lake of Wuhan (Yang et al., 2005) where the NP concentration was up to 119100 ng/g dw, the river sediments from the PRD is the most APs-contaminated sediments in China. The sedimentary APs levels in the PRD are also much higher than those in Jiaozhou Bay and its surrounding rivers (Fu et al., 2007) and Lanzhou Reach of Yellow River (Xu et al., 2006), and slightly higher than those in Wenyu river of Beijing (Lei et al., 2008). The BPA concentrations in the river sediments in the PRD are similar to those of APs, and are significantly higher than those of other aquatic sediments in China, except for those of the Donghu Lake. For the steroid estrogens, however, few data are available so far in the aquatic sediments in China (Table 2).

In comparison with other overseas investigations, the sedimentary concentrations of APs in this study fell in the high value ranges of the world (Table 2). Apparently the pollution levels of APs in the river sediments are higher in the PRD than in Korea, Germany, Spain, and Netherlands, while they are close to the concentration ranges in urban and industrial zones and their adjacent areas located in Japan, US, UK, and Canada. The BPA concentration ranges are also in the high value scope, and similar to those in Elbe River, Germany (Heemken et al., 2001), and Tyne and Tees estuaries, UK

Table 2
Comparison of concentration ranges of EDCs in surface sediments around the world.

Location	Concentration (ng/g dw)					Reference
	OP	NP	BPA	E1	E2	
Rivers from the PRD, China	<2.0–210	107–16198	<1.7–429.5	<1.3–10.9	<0.9–2.6	This study
Rivers from the PRD, China	1.0–93	110–7808				Chen et al. (2006)
Jiaozhou Bay, China	<0.7–3.6	3.6–299	<0.7–20.3			Fu et al. (2007)
Surrounding rivers of Jiaozhou Bay, China	1.6–146	23.8–3970	<2.4–27.3			Fu et al. (2007)
Lanzhou Reach of Yellow River, China		38.9–863				Xu et al. (2006)
Wenyuhe river of Beijing, China		124.5–8157.9		0.6–59.6		Lei et al. (2008)
Donghu Lake of Wuhan, China		5460–119100		990–3420		Yang et al. (2005)
Han River, Korea		25.4–932				Li et al. (2004a,b)
Lake Shihwa, Korea		93–859				Li et al. (2004a,b)
Ulsan Bay and its inland, Korea	<1.0–120	<1.0–1040	<1.0–53.5			Khim et al. (2001)
Masam Bay, Korea	3.97–179	113–3890	2.7–50.3			Khim et al. (1999)
Sumidagawa and Tamagawa river, Japan	3.0–670	30–13000				Isobe et al. (2001)
Tokyo Bay, Japan	6.0–10	120–640		0.05–3.6	nd[a]–0.59	Isobe et al. (2001 and 2006)
Lake Teganuma, Japan		11.8–21000		<0.05–3.5		Mibu et al. (2004)
Rivers, UK			<3.4–9	<0.9–3	<0.9–4	Liu et al. (2004)
Ouse river, UK				0.4–28.8	0.97	Labadie et al. (2007)
Nene and Lea river, UK				0.04–0.39	nd	Williams et al. (2003)
Tyne and Tees estuaries, UK	2–340	30–9050				Lye et al. (1999)
Rivers and estuaries, UK		<LOD[b]–15000				Blackburn et al. (1999)
Elbe River, Germany	21–86	367–997	70–340			Heemken et al. (2001)
Rivers, Germany			10–190			Fromme et al. (2002)
Baden–Wurttemberg rivers and streams, Germany	<0.5–8	10–259	<0.5–15			Bolz et al. (2001)
Rivers, Germany				<0.2–2	<0.2–1.5	Ternes et al. (2002)
Rivers, US		<LOD–2960				Naylor et al. (1992)
Jamaica Bay, US	nd–45	6.99–13700				Ferguson et al. (2001)
Cuyahoga river, US		75–340				Rice et al. (2003)
Rivers, Spain				<0.5–11.9	<1.0	López de Alda et al. (2002)
Rivers, Spain	15–104	20–655		nd–11.8	nd	Petrovic et al. (2002)
Rhine and Scheldt estuaries, Netherlands		<LOD–1080				Jonkers et al. (2003)
Great Lake and St. Lawrence rivers, Canada	nd–1800	170–72000				Bennie et al. (1997)
TiberRiver, Italy		50–970	<3.0			Patrolecco et al. (2004)

[a] Not detected.
[b] Limit of detection.

(Lye et al., 1999), and higher than those of the other investigated European rivers. The concentrations of natural estrogen E1 in the sediments of the PRD are at high levels as well, and similar to those in the Spanish rivers (López de Alda et al., 2002), and lower than those in Ouse River of UK, but higher than those in Japanese and the other investigated European rivers. Additionally the E2 concentrations in the sediments of the PRD are in the same range as those of the overseas studies (Table 2).

In a word, the rivers from the PRD were heavily contaminated by phenolic xenoestrogens and became one of the seriously polluted regions by APs and BPA in the world.

4. Conclusion

In summary, phenolic xenoestrogens were the dominant contaminates of the EDCs pollution in the surface sediments of the rivers from the PRD, and were primarily attributed to local domestic sewages and industrial effluent discharge. The positive correlations between the EDCs concentrations and the TOC contents demonstrated that the sedimentary organic carbon played an important role in the sorption and distribution of EDCs. Compared with other investigations, the concentration ranges of APs and BPA fell in the high value scope in the world, and the concentrations of the natural estrogens E1 and E2 were similar to those of the other overseas observations, indicating that the river in ZR and DR from the PRD became one of the most heavily polluted regions by phenolic xenoestrogens in the world.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.marpolbul.2011.01.026.

References

Ahel, M., Giger, W., 1993. Partitioning of alkylphenols and alkylphenol polyethoxylates between water and organic solvents. Chemosphere 26, 1471–1478.

Bennie, D.T., Sullivan, C.A., Lee, H.B., Peart, T.E., Maguire, R.J., 1997. Occurrence of alkylphenols and alkylphenol mono- and diethoxylates in natural waters of the Laurentian Great Lakes basin and the upper St. Lawrence River. Science of the Total Environment 193, 263–275.

Blackburn, M.A., Kirby, S.J., Waldock, M.J., 1999. Concentrations of alkylphenol polyethoxylates entering UK estuaries. Marine Pollution Bulletin 38, 109–118.

Bolz, U., Hagenmaier, H., Korner, W., 2001. Phenolic xenoestrogens in surface water, sediments, and sewage sludge from Baden–Wurttemberg, South-west Germany. Environmental Pollution 115, 291–301.

Burkhardt-Holm, P., Giger, W., Güttinger, H., Ochsenbein, U., Peter, A., Scheurer, K., Suter, M.J.F., Ochsenbein, U., Segner, H., Staub, E., 2005. Where have all the fish gone. Environmental Science and Technology 39, 441A–447A.

Chen, B., Duan, J.C., Mai, B.X., Luo, X.J., Yang, Q.S., Sheng, G.Y., Fu, J.M., 2006. Distribution of alkylphenols in the Pearl River Delta and adjacent northern South China Sea, China. Chemosphere 63, 652–661.

Ferguson, P.L., Iden, C.R., Brownwell, B.J., 2001. Distribution and fate of neutral alkylphenol ethoxylate metabolites in a sewage-impacted urban estuary. Environmental Science and Technology 35, 2428–2435.

Fromme, H., Küchler, T., Otto, T., Pilz, K., Müller, J., Wenzel, A., 2002. Occurrence of phthalates and bisphenol A and F in the environment. Water Research 36, 1429–1438.

Fu, M.Z., Li, Z.Y., Gao, H.W., 2007. Distribution characteristics of nonylphenol in Jiaozhou Bay of Qingdao and its adjacent rivers. Chemosphere 69, 1009–1016.

Gao, Q., Tao, Z., Shen, C., Sun, Y., Yi, W., Xing, C., 2002. Riverine organic carbon in the Xijiang River (South China): seasonal variation in content and flux budget. Environmental Geology 41, 826–832.

Gong, J., Ran, Y., Chen, D., Ma, X., Yang, Y., 2009. Occurrence and environmental risk of endocrine-disrupting chemicals in surface waters of the Pearl River, South China. Environmental Monitoring Assessment 156, 199–210.

Hale, R.C., Smith, C.L., de Fur, P.O., Harvey, E., Bush, E.O., la Gaurdia, M.L., Vadas, G.G., 2000. Nonylphenols in sediments and effluents associated with diverse wastewater outfalls. Environmental Toxicology and Chemistry 19, 945–952.

Heemken, O.P., Reincke, H., Stachel, B., Theobald, N., 2001. The occurrence of xenoestrogens in the Elbe River and the North Sea. Chemosphere 45, 245–259.

Irwin, L.K., Gray, S., Oberdorster, E., 2001. Vitellogenin induction in painted turtle, *Chrysemys picta*, as a biomarker of exposure to environmental levels of estradiol. Aquatic Toxicology 55, 49–60.

Isobe, T., Nishiyama, H., Nakashima, A., Takada, H., 2001. Distribution and behavior of nonylphenol, octylphenol, and nonylphenol monoethoxylate in Tokyo metropolitan area: their association with aquatic particles and sedimentary distributions. Environmental Science and Technology 35, 1041–1049.

Isobe, T., Serizawa, S., Horiguchi, T., Shibata, Y., Managaki, S., Takada, H., Morita, M., Shiraishi, H., 2006. Horizontal distribution of steroid estrogens in surface sediments in Tokyo Bay. Environmental Pollution 144, 632–638.

Jobling, S., Nolan, M., Tyler, C.R., Brighty, G., Sumpter, J.P., 1998. Widespread sexual disruption in wild fish. Environmental Science and Technology 32, 2498–2506.

Jobling, S., Sheahan, D., Osborne, J.A., Matthiessen, P., Sumpter, J.P., 1996. Inhibition of testicular growth in rainbow trout (*Oncorhynchus mykiss*) exposed to estrogenic alkylphenolic chemicals. Environmental Toxicology and Chemistry 15, 194–202.

John, D.M., House, W.A., White, G.F., 2000. Environmental fate of nonylphenol ethoxylates: differential adsorption of homologs to components of river sediment. Environmental Toxicology and Chemistry 19, 293–300.

Jonkers, N., Laane, R.P.M., de Voogt, P., 2003. Fate of nonylphenol ethoxylates and their metabolites in two Dutch estuaries: evidence of biodegradation in the field. Environmental Science and Technology 37, 321–327.

Khim, J.S., Kannan, K., Villeneuve, D.L., Koh, C.-H., Giesy, J.P., 1999. Characterization and distribution of trace organic contaminants in sediment from Masan Bay, Korea. 1. Instrumental analysis. Environmental Science and Technology 33, 4199–4205.

Khim, J.S., Lee, K.T., Kannan, K., Villeneuve, D.L., Giesy, J.P., Koh, C.H., 2001. Trace organic contaminants in sediment and water from Ulsan Bay and its vicinity, Korea. Archives of Environmental Contamination and Toxicology 40, 141–150.

Kidd, K.A., Blanchfield, P.J., Mills, K.H., Palace, V.P., Evans, R.E., Lazorchak, J.M., Flick, R.W., 2007. Collapse of a fish population after exposure to a synthetic estrogen. Proceeding of the National Academy of Sciences 104, 8897–8901.

Labadie, P., Cundy, A., Stone, K., Andrews, M., Valbonesi, S., Hill, E., 2007. Evidence for the migration of steroidal estrogens through river bed sediments. Environmental Science and Technology 41, 4299–4304.

Lai, K.M., Johnson, K.L., Scrimshaw, M.D., Lester, J.N., 2000. Binding of waterborne steroid estrogens to solid phases in river and estuarine systems. Environmental Science and Technology 34, 3890–3894.

Lei, B.L., Luo, J.P., Zha, J.M., Huang, S.B., Liu, C., Wang, Z.J., 2008. Distribution of nonylphenols and bisphenol-A in the sediments of Wenyuhe river. Environmental Chemistry 27, 314–317 (in Chinese).

Levy, G., Lutz, I., Krüger, A., Kloas, W., 2004. Bisphenol A induces feminization in *Xenopus laevis* tadpoles. Environmental Research 94, 102–111.

Li, D., Kim, M., Shim, W.J., Yim, U.H., Oh, J.R., Kwon, Y.J., 2004a. Seasonal flux of nonylphenol in Han River, Korea. Chemosphere 56, 1–6.

Li, Z., Li, D., Oh, J.R., Je, J.G., 2004b. Seasonal and spatial distribution of nonylphenol in Shihwa Lake, Korea. Chemosphere 56, 611–618.

Lin, H., Han, W., 2001. Water quality assessment and analysis before and after the decade of the dry period in Lingdingyang estuary of the Pearl River Mouth. Marine Environmental Science 20, 28–31 (in Chinese).

Liu, R., Zhou, J.L., Wilding, A., 2004. Microwave-assisted extraction followed by gas chromatography–mass spectrometry for the determination of endocrine disrupting chemicals in river sediments. Journal of Chromatography A 1038, 19–26.

López de Alda, M.J., Gil, A., Paz, E., Barceló, D., 2002. Occurrence and analysis of estrogens and progestogens in river sediments by liquid chromatography–electrospray–mass spectrometry. Analyst 127, 1299–1304.

Lye, C.M., Frid, C.L.J., Gill, M.E., Cooper, D.W., Jones, D.M., 1999. Estrogenic alkylphenols in fish tissues, sediments, and waters from the UK Tyne and Tees estuaries. Environmental Science and Technology 33, 1009–1014.

Mibu, K., Wada, J., Okayasu, Y., Tsumori, J., Komori, K., Tanaka, H., Li, J.H., Sasaki, M., Sato, C., 2004. Distribution of estrogen, nonylphenol and its derivatives in the sediments of a shallow lake. Water Science and Technology 50, 173–179.

Naylor, C.G., Mieure, J.P., Adams, W.J., Weeks, J.A., Castaldi, F.J., Ogle, L.D., Romano, R.R., 1992. Alkylphenol ethoxylates in the environment. Journal of the American Oil Chemists Society 69, 695–703.

Oehlmann, J., 2000. Effects of endocrine disruptors on prosobranch snails (Mollusca: Gastropoda) in the laboratory. Part l: bisphenol a and octylphenol as xenoestrogens. Ecotoxicology 9, 383–397.

Patrolecco, L., Capri, S., de Angelis, S., Polesello, S., Valsecchi, S., 2004. Determination of endocrine disrupting chemicals in environmental solid matrices by extraction with a non-ionic surfactant (Tween 80). Journal of Chromatography A 1022, 1–7.

Peng, X., Yu, Y., Tang, C., Tan, J., Huang, Q., Wang, Z., 2008. Occurrence of steroid estrogens, endocrine-disrupting phenols, and acid pharmaceutical residues in urban riverine water of the Pearl River Delta, South China. Science of the Total Environment 397, 158–166.

Petrovic, M., Sole, M., López de Alda, M.J., Barcelo, D., 2002. Endocrine disruptors in sewage treatment plants, receiving river waters, and sediments: integration of chemical analysis and biological effects on feral carp. Environmental Toxicology and Chemistry 21, 2146–2156.

Ran, Y., Huang, W.L., Rao, P.S.C., Liu, D.H., Fu, J.M., Sheng, G.Y., 2002. The role of condensed organic matters in the nonlinear sorption of hydrophobic organic contaminants by peat and sediments. Journal of Environmental Quality 31, 1953–1962.

Rice, C.P., Schmitz-Afonso, J.S., Loyo-Rosales, J.E., Link, E., Thoma, R., Fay, L., Altfater, D., Camp, M.J., 2003. Alkylphenol and alkylphenol–ethoxylates in carp, water and sediment from the Cuyahoga River, Ohio. Environmental Science and Technology 37, 3447–3754.

Routledge, D., Sheahan, C., Desbrow, G.C., Brighty, M., Waldock, Sumpter, J.P., 1998. Identification of estrogenic chemicals in STW effluent. 2. In vivo responses in trout and roach. Environmental Science and Technology 32, 1559–1565.

Snyder, S.A., Keith, T.L., Verbrugge, D.A., Snyder, E.M., Gross, T.S., Kannan, K., Giesy, J.P., 1999. Analytical methods for detection of selected estrogenic compounds in aqueous mixtures. Environmental Science and Technology 33, 2814–2820.

Staples, C.A., Dorn, P.B., Klecka, G.M., O'Block, S.T., Harris, L.Y., 1998. A review of the environmental fate, effects and exposures of bisphenol A. Chemosphere 36, 2149–2173.

Ternes, T.A., Andersen, H., Gillberg, D., Bonerz, M., 2002. Determination of estrogens in sludge and sediments by liquid extraction and GC/MS/MS. Analytical Chemistry 74, 3498–3504.

Tsuda, T., Takino, A., Kojima, M., Harada, H., Muraki, K., Tsuji, M., 2000. 4-Nonylphenols and 4-tert-octylphenol in water and fish from rivers flowing into Lake Biwa. Chemosphere 41, 757–762.

Williams, R.J., Johnson, A.C., Smith, J.J.L., Kanda, R., 2003. Steroid estrogen profiles along river stretches arising from sewage treatment works discharges. Environmental Science and Technology 37, 1744–1750.

Xu, J., Wang, P., Guo, W., Dong, J., Wang, L., Dai, S., 2006. Seasonal and spatial distribution of nonylphenol in Lanzhou Reach of Yellow River in China. Chemosphere 65, 1445–1451.

Yang, F.X., Xu, Y., Pfister, G., Henkelmann, B., Schramm, K.W., 2005. Nonylphenol, bisphenol-A and DDTs in Lake Donghu, China. Fresenius Environmental Bulletin 14, 173–180.

Ying, G.G., Williams, B., Kookana, R., 2002. Environmental fate of alkylphenols and alkylphenol ethoxylates – A review. Environmental International 28, 215–226.