Analysis and occurrence of typical endocrine-disrupting chemicals in three sewage treatment plants

L. Y. Wang, X. H. Zhang and N. F. Y. Tam

ABSTRACT

Seven typical endocrine-disrupting chemicals (EDCs), including bisphenol A (BPA), 4-tert-octylphenol (OP), estrone (E1), estradiol (E2), 17α-estradiol (17α-E2), estriol (E3) and 17α-ethinylerstradiol (EE2) in wastewater, were simultaneously determined with gas chromatography–mass spectrometry (GC–MS). Samples, including influents, effluents and wastewater of different unit processes, were taken seasonally from three different sewage treatment plants. The result showed that BPA and EE2 were the two main types of EDCs in all the samples. The average concentration of BPA were in the range of 268.1–2,588.5 ng l⁻¹ in influents and 34.0–3,099.6 ng l⁻¹ in effluents, while EE2 ranging from 133.1 to 403.2 ng l⁻¹ and from 35.3 to 269.1 ng l⁻¹, respectively. Seasonal change of EDCs levels in effluents was obvious between wet season and dry season. Besides, BPA and E3 could be effectively removed by the biological treatment processes (oxidation ditch and A²/O) with the unit removal of 64–91% and 63–100% for each compound, while other five EDCs had moderate or low removal rates. The study also proved that physical treatment processes, including screening, primary sedimentation and pure aeration, had no or little effect on EDCs removal.

Key words | endocrine disrupting chemicals, estradiol, estriol, ethynylestradiol, sewage treatment

INTRODUCTION

Endocrine-disrupting chemicals (EDCs) are exogenous substances that can mimic or antagonize the actions of endogenous hormones in the endocrine system, affecting the health of humans and wild lives. Feminization or intersex of aquatic animals has been observed and attributed to the EDCs in the environment (Harrises et al. 1997; Jobling et al. 1998; Hashimoto et al. 2000). Actually, most of the EDCs, such as bisphenol A (BPA) and alkylphenols (APs), are introduced into the environment by human activities. Among the most estrogenic chemicals, natural or synthesized steroid hormones have received great attention since 1990s due to their strong endocrine-disrupting potency even at low concentration, the ng l⁻¹ level (Purdom et al. 1994). These reported compounds include 17β-estradiol (E2) and less active estrone (E1), estriol (E3), 17α-estradiol (17α-E2) and 17α-ethinylerstradiol (EE2). These compounds have been considered as the main contributors to the estrogenic activity observed in aquatic systems receiving sewage treatment plant effluents (Desbrow et al. 1998; Larsson et al. 1999; Matsui et al. 2000).

So far, analytical methods for the quantification of EDCs, including alkylphenols, BPA, conjugated and free estrogens, in different environmental matrices have been developed (Lopez de Alda & Barcelo 2001; Peng et al. 2006). A typical procedure for estrogen determination in water phase includes filtration, extraction (or concentration), clean-up, derivatization and detection by gas chromatography with mass spectrometry (GC–MS). As most important source and transport routes of EDCs, many reports have been published on EDCs investigation in sewage treatment plants (STPs) (Belfroid et al. 1999; Ternes et al. 1999; Johnson et al. 2000; Fuerhacker 2003;
Reported levels of selected estrogens, including E1, E2, E3 and EE2, varied between several to dozens ngL$^{-1}$ in STP effluents. The levels of EDCs in STPs of China were reported higher than that of other countries under investigation (Lee et al. 2006; Jin et al. 2008). Besides, different removal rates of EDCs in STPs have been reported, depending on the treatment processes (Ternes et al. 1999; Baronti et al. 2000; Nasu et al. 2000; Braga et al. 2005).

For instance, Braga et al. (2005) found that the enhanced STP was mostly ineffective in removing these steroids, while the biological process played a more important role than adsorption.

In the present study, the distribution and seasonal variations of seven typical EDCs, including 4-tert-octylphenol (OP), bisphenol A (BPA), estrone (E1), 17β-estradiol (E2), 17α-estradiol (17α-E2), estriol (E3) and 17α-ethinylestradiol (EE2) in three typical sewage treatment plants located in South China were investigated using solid phase extraction method followed by gas chromatography–mass spectrometry (SPE–GC–MS) analysis. The removal efficiency of EDCs in different unit processes was also determined.

**MATERIALS AND METHODS**

**Sampling sites and sample collection**

Three STPs, two secondary sewage treatment plants (A and B) and a coastal primary treatment plant (C), located in the south of China and served more than 2 million people in Shenzhen, were investigated in the present study. Basic information in each plant was shown in Table 1 and their treatment processes were summarized in Figure 1. The plant A was divided into two stages which consisted of secondary treatment processes of anaerobic–anoxic–oxic (AAO) and triple oxidation ditch, respectively. The flow scheme of plant B also consisted of oxidation ditch which was similar to that of the second stage in plant A. Different from plants A and B, only primary sewage treatment process was installed in plant C (primary sedimentation). To assess the removal rates of different unit operations in different seasons, the influents, effluents, and sewage from the outlets of the unit chambers were collected every three month during the period from March 2008 to January 2009. The sampling dates were March 31 (dry season), June 16 (wet season), August 21 (wet season) of the year 2008 and January 10, 2009 (dry season). Before sampling, all the glass wares were washed with hexane for three times to remove residual organic chemicals, and washed with ultra pure water before in use. When sampling, the bottle was filled up and no headspace was left. For each time, a grab sample of 1 l was taken in the morning (between 9:00 and 11:00 AM). The pH value of samples was adjusted to about 3.0 with hydrochloric acid. Water samples were then filtrated through micro membranes (GF/B, Whatman, USA) and filtrates kept at 4°C for no more than 24 h before further pretreatment.

**Materials and standards**

Standard chemicals, including bisphenol A (BPA), 4-tert-octylphenol (OP), estrone (E1), 17β-estradiol (17β-E2), 17α-estradiol (17α-E2), estriol (E3), 17α-ethinylestradiol (EE2), were purchased from Dr. Ehrenstorfer (Augsburg, Germany). Deuterated estradiol (E2-d2) and 17β-estradiol-acetate (E2-AC) were obtained from Sigma-Aldrich (USA, > 99%). The E2-d2 was used as surrogate standard and E2-acetate as internal standard for quantification of EDCs.

<table>
<thead>
<tr>
<th>Sites</th>
<th>Population equiv</th>
<th>Daily flow (m$^3$)</th>
<th>SS (mg/l)</th>
<th>BOD (mg/l)</th>
<th>COD (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Influent</td>
<td>Effluent</td>
<td>Influent</td>
</tr>
<tr>
<td>STP-A</td>
<td>650,000</td>
<td>350,000</td>
<td>630</td>
<td>10</td>
<td>185</td>
</tr>
<tr>
<td>STP-B</td>
<td>450,000</td>
<td>300,000</td>
<td>340</td>
<td>16</td>
<td>240</td>
</tr>
<tr>
<td>STP-C</td>
<td>1,216,800</td>
<td>530,000</td>
<td>380</td>
<td>100</td>
<td>150</td>
</tr>
</tbody>
</table>

SS: suspended solid; BOD: biochemical oxygen demand; COD: chemical oxygen demand.

The value of SS, BOD and COD are average levels of the year of 2008.
Stock solutions dissolved in methanol were prepared every three months with a concentration of 1.0 g l\(^{-1}\). All the organic solvents, including hexane, methanol and Methyl Tertiary Butyl Ether (MTBE), were of pesticide grade. Milli-Q water was used during all the procedures.

**Solid phase extraction (SPE)**

Before conducting solid phase extraction, the cartridge (Oasis HLB, 5 cc, 200 mg, Waters, USA) was conditioned sequentially with 5 ml MTBE, 5 ml Methanol, and 5 ml ultra pure water. After conditioning, water sample spiked with 200 ng E2-d2 was loaded through cartridge at the speed of 10 ml min\(^{-1}\). Following the concentration, the cartridge was washed sequentially with 5 ml methanol (40%), 5 ml pure water and 5 ml methanol/NH\(_4\)OH (10%/2%). Finally, the target chemicals were eluted from the cartridge by 10 ml elution solution (MTBE: methanol, 9:1). Simultaneously, the clean-up procedure was carried out by putting the silica gel cartridge (SEP-PAK plus silica, Waters, USA), which was preconditioned by 5 ml hexane, just below the Oasis HLB cartridge and collecting the eluate with a glass vial. The collected eluates (adding 200 ng E2-AC as internal standard) were then evaporated to dry with nitrogen purge and ready for the derivatization.

**Derivatization**

The derivatization was carried out with N, O-bis (trimethylsilyl) trifluoroacetamide (BSTFA) including 1% trimethylchlorosilane (TMCS) (Supelco, USA). By adding 100 μl BSTFA and 50 μl pyridine, the tube containing the analyte was kept at 70°C for one hour. The derivatized product was then directly analyzed by GC–MS.

**GC–MS analysis**

GC–MS (QP 2010-Plus, Shimadzu, Japan) with a capillary column (Rxi-5 ms, 30 m × 0.25 mm × 0.25 μm) was used to determine the selected eight EDC derivatives simultaneously. The GC oven temperature was programmed at 100°C for 1.0 min and then 13°C per minute to 200°C, 16°C per minute to 265°C, 5°C per minute to 290°C, final hold for 2.0 min. The whole program lasted about 23.00 min. The GC–MS interface heater, the ion source, and injection port temperatures were maintained at 280°C, 250°C and 280°C, respectively. The MS analysis was performed with an EI source and selective ion mode (SIM). The \(m/z\) values used for quantification and qualification were shown in Table 2.

**Quality assurance and quality control (QA/QC)**

By using E2-d2 as a surrogate standard and E2-acetate as an internal standard, the calibration curve of the internal method was obtained by analyzing a batch of working solutions with concentrations from 10 to 1,000 ng ml\(^{-1}\). Instrumental limits of detection (LOD) were estimated at...

<table>
<thead>
<tr>
<th>Compound</th>
<th>Retention time (min)</th>
<th>Molecular weight</th>
<th>(m/z) used for qualification</th>
<th>(m/z) used for quantification</th>
</tr>
</thead>
<tbody>
<tr>
<td>OP</td>
<td>10.2</td>
<td>206.3</td>
<td>292.00</td>
<td>179.00</td>
</tr>
<tr>
<td>BPA</td>
<td>13.0</td>
<td>228.3</td>
<td>372.00</td>
<td>357.00</td>
</tr>
<tr>
<td>17α-E2</td>
<td>16.4</td>
<td>272.4</td>
<td>416.00, 326.00</td>
<td>285.00</td>
</tr>
<tr>
<td>E1</td>
<td>16.4</td>
<td>270.4</td>
<td>257.00, 218.00</td>
<td>342.00</td>
</tr>
<tr>
<td>E2</td>
<td>16.9</td>
<td>272.4</td>
<td>416.00, 326.00</td>
<td>285.00</td>
</tr>
<tr>
<td>E2-d2</td>
<td>17.0</td>
<td>273.4</td>
<td>287.00, 234.00</td>
<td>418.00</td>
</tr>
<tr>
<td>E2-acetate</td>
<td>17.9</td>
<td>314.0</td>
<td>244.00, 297.00</td>
<td>386.00</td>
</tr>
<tr>
<td>EE2</td>
<td>18.2</td>
<td>296.4</td>
<td>285.00, 440.00</td>
<td>425.00</td>
</tr>
<tr>
<td>E3</td>
<td>19.4</td>
<td>288.4</td>
<td>504.00, 386.00</td>
<td>311.00</td>
</tr>
</tbody>
</table>
a signal-to-noise ratio of 3 and limits of quantification (LOQ) were set at 10-fold of LOD. For recovery determination, the raw sewage, effluents were spiked with stock standard solution containing each EDC of 200 ng and with E2-d2 of 200 ng. Three spike-recovery experiments were applied to each kind of sample and the recovery with standard deviation were determined. When analyzing the real samples, E2-d2 and E2-acetate were added to all samples for EDCs quantification and the recovery of E2-d2 was used to assess the accuracy of the determination.

**RESULTS AND DISCUSSION**

Detection limits and recoveries of the SPE–GC–MS method

The limits of detection (LOD) for the target EDCs were estimated in the range of 0.3–1.2 ng ml\(^{-1}\) for injection and the method limits of quantification (LOQ) were found to be in the range of 3.0–12.0 ng ml\(^{-1}\) for injection (Table 3). For the recovery of EDCs, mean values were in the range of 63.5–123.9% depending on the property of water sample and EDC types. The recovery of E2-d2, which was used as a surrogate standard to indicate the recovery of the selected EDCs, was in the range of 78.5–98.0% and was a good indicator for the EDCs recoveries.

Levels of EDCs in influents and effluents of the three STPs

The average concentrations of seven typical EDCs in influents and effluents of the three STPs were summarized in Table 4. It was shown that the average concentrations of BPA in influents were 268.1, 2,224.9 and 2,588.5 ng l\(^{-1}\), respectively in STP-A, STP-B and STP-C. While BPA concentrations in effluents were 34.0, 272.8 and 3,099.6 ng l\(^{-1}\), respectively. The study results were higher than those reported in the literature (Fuerhacker 2003). The average concentration of EE2 were in the range of 133.1–403.2 ng l\(^{-1}\) in influents and 35.3–269.1 ng l\(^{-1}\) in effluents, which were much higher than other reported results (Andersen et al. 2003; Braga et al. 2005). Besides of BPA and EE2, other five selected EDCs, including OP, 17α-E2, E1, E2 and E3, were at the average level of lower than 70 ng/l. Particularly, OP and 17α-E2 were in the range of ND to 17.4 ng l\(^{-1}\) (ND means not detected or lower than detection limit). By comparing concentrations of EDCs in influents and effluents of the three STPs, the overall removal of the wastewater treatment processes was evaluated. As shown in Table 4, for STP-A, the removal rates of OP, BPA, E1, EE2 and E3 were 31, 87, 71, 84, 64%, respectively, while the removal rates of 17α-E2 and E2 were relatively low. Compared with STP-A, STP-B had similar removal rates for OP (41%), BPA (88%) and E3 (78%), but relatively low removal for E1 (14%) and EE2 (25%). With very different unit processes (only enhanced primary treatment) from the first two STPs, STP-C can not remove all investigated EDCs effectively except that E1 (49%) and EE2 (33%) were partly removed in the process. One thing should be noticed that the grab sample was collected randomly in the morning and only the dissolved proportion in the sample was detected, as a result, more comprehensive study need to be conducted to get more detailed information.

BPA and EE2 were the two main types of EDCs in the present study, while previous researchers showed that

**Table 3** | Accuracy and sensitivity of the analytical method with GC–MS for EDCs measurement

<table>
<thead>
<tr>
<th>EDC</th>
<th>OP</th>
<th>BPA</th>
<th>17α-E2</th>
<th>E1</th>
<th>E2</th>
<th>EE2</th>
<th>E3</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOD(^{a}) (ng ml(^{-1}))</td>
<td>0.4</td>
<td>0.45</td>
<td>0.6</td>
<td>0.45</td>
<td>0.58</td>
<td>1.05</td>
<td>1.20</td>
</tr>
<tr>
<td>LOQ(^{b}) (ng ml(^{-1}))</td>
<td>4.0</td>
<td>4.5</td>
<td>6.0</td>
<td>4.5</td>
<td>5.8</td>
<td>10.5</td>
<td>12.0</td>
</tr>
<tr>
<td>Recovery (%) for raw sewage(^{c})</td>
<td>63.5 ± 6.7</td>
<td>123.9 ± 4.4</td>
<td>67.7 ± 9.8</td>
<td>68.5 ± 3.3</td>
<td>70.4 ± 5.3</td>
<td>84.0 ± 5.3</td>
<td>72.2 ± 1.3</td>
</tr>
<tr>
<td>Recovery (%) for effluent</td>
<td>87.9 ± 2.4</td>
<td>98.9 ± 10.5</td>
<td>86.3 ± 4.0</td>
<td>70.8 ± 6.5</td>
<td>72.3 ± 4.0</td>
<td>76.8 ± 7.8</td>
<td>86.9 ± 3.2</td>
</tr>
</tbody>
</table>

\(^{a}\)LOD: limit of detection.

\(^{b}\)LOQ: limit of quantification.

\(^{c}\)Recovery value represents the mean and standard deviation of three replicates.
estrone, usually the primary metabolite of estradiol, was the main estrogen form in the effluents of STPs and surface waters (D’Ascenzo et al. 2003; Labadie & Budzinski 2005).

Table 4 showed that EE2 concentration was extremely high compared with other natural estrogens, including E1, E2, E3 and 17α-E2. Most of the previous research reported EE2 ranging from ND (not detected) to 42 ng l$^{-1}$ (Desbrow et al. 1998; Belfroid et al. 1999; Ternes et al. 1999; Jin et al. 2008), while Tabak et al. (1981) reported levels of EE2 around 1 μg l$^{-1}$ in raw sewage and effluents from several STPs in the USA. Compared with other estrogens, EE2 has relatively higher Kow value than other natural steroids, which could support the fact that EE2 was more persistent to biodegradation (Layton et al. 2000) and consequently result in accumulation in the system. Laboratory studies on the estrogenic potency of EE2 demonstrated that levels as low as 1 to 10 ng l$^{-1}$ could generate the response shown by the caged fish feed in STP effluent (Purdom et al. 1994). In this study, the average EE2 concentration in the effluents in STP-A, STP-B and STP-C reached 35.3, 99.1 and 269.1 ng l$^{-1}$, respectively, and the level of EE2 in raw sewage was even higher, with a maximum value of 895.5 ng l$^{-1}$. The problem of EE2 pollution in natural water bodies receiving sewage effluents in the area of China south must be seriously addressed.

STP-C with just enhanced primary sedimentation treatment unit had significantly lower removal of EDCs than the STP-A and STP-B (Table 4). Braga et al. (2005) also found that the enhanced primary STP was mostly ineffective at removing the steroids. Even though the removal rates of EDCs depended greatly on the performance of unit operation and raw sewage quality, the average removal rates of EDCs in the present study were lower than that in other reports (Braga et al. 2005).

Seasonal fluctuation of EDCs concentration in the STPs

The total concentrations of EDCs in the effluents collected in dry season were about two to five-fold higher than that in wet season (Figure 2). In wet season, total values of the six
selected EDCs (OP, 17α-E2, E1, E2, E3, EE2) in STP-A, STP-B and STP-C were 51.5, 97.4 and 250.6 ng l\(^{-1}\), respectively, while the respective values in dry season were 193.6, 500.1 and 608.5 ng l\(^{-1}\). A similar trend of having higher values in dry than in wet seasons was also observed for BPA, its concentrations in three STPs were 29.4, 148.4 and 379.2 ng l\(^{-1}\) in wet season; 43.2, 668.9 and 8,540.4 ng l\(^{-1}\) in dry season. The monthly flux of the three STPs of the investigated period was shown in Figure 3. The average monthly flow rates of STP-A, STP-B and STP-C were 7.8\(^{\pm}\)1.3, 6.2\(^{\pm}\)0.6 and 15.9\(^{\pm}\)0.7 million m\(^{3}\) per month, respectively. All the three plants were in full load operation most of the time. In wet season, rainfall mixed into the municipal wastewater and large amounts of the wastewater carrying EDCs were directly discharged into receiving water by overflow and cause great environmental risk which should be paid close attention.

According to the monthly rainfall in Figure 4, the total precipitation of wet season (from April to October) was around 2,600 mm in 2008, while the value was only 123 mm of dry season (Jan., Feb., Mar., Nov., Dec. of 2008 and Jan. of 2009). Precipitation in June of 2008 was extremely high at 1,395.3 mm, which was around 4.7 times higher than the corresponding average data of last 30 years. The rain water can dilute the sewage to a great extent and result in a decrease of EDCs concentration in sewage. Some researchers, who focused on behavior of EDCs in STPs or surface waters, also reported the various concentrations and removal rates of EDCs in different seasons, especially summer and winter, and concluded that varied temperature may affect the biodegradation process to a large degree (Matsuoka et al. 2005; Jin et al. 2008). In the present study, the rain water dilution effect should be more important than water temperature as temperature variation between summer and winter seasons in the sampling sites were in small ranges throughout the year (Figure 4, around 22 \(\pm\) 6°C).

### EDC removal in different treatment processes

The removal rates of EDCs varied among different treatment processes, including AAO operation, oxidation ditch and primary treatment (Table 5). It was shown that primary treatment processes, including sedimentation and aeration, was ineffective to remove all investigated EDCs with unit removal rates fluctuated from negative removal (minus value) to 51%. Four biological processes including AAO and three oxidation ditches were also investigated in the study. In STP-A, E3 and BPA was effectively removed by the biological treatment processes including AAO and oxidation ditch, with the removal rates of 81–100% for E3 and 82–91% for BPA. Meanwhile, removal efficiencies of E3 and BPA in oxidation ditches of STP-B were also very high in the range of 63–93% and 64–87%, respectively. EE2 was removed with moderate efficiency (50–77%) by the oxidation ditches in STP-B, while the biological processes (AAO and oxidation ditch) in STP-A showed slightly better performance in removing EE2 (62–100% and 64–94%, respectively). OP also showed moderate removal in AAO and oxidation ditch processes with the removal rates of 29–78% and 21–67%. 17α-E2, one of natural estrogens with low concentration, can not be removed effectively. Compared with other estrogens, the removal efficiency of E1 and E2 by

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**Figure 2** Average levels of EDCs in effluents of the three STPs for different seasons (wet season: from April to October; dry season: from November to March).

**Figure 3** Monthly flow rates of three STPs in the investigated period.
activated sludge systems was variable. Removal efficiency of E1 in AAO process was in the range of 52–66% while the removal decreased in the range of 10–52% in all three oxidation ditches. E2 removal in AAO and oxidation ditch of STP-A was in the range of 13–32% and 15–18%, respectively, while other two parallel oxidation ditches in STP-B can remove 42–78% of E2.

It has been proved that biological process was effective in removing EDCs from wastewater (Ternes et al. 1999; Baronti et al. 2000; Braga et al. 2005) and the result of this study also support this point, especially for E3 and BPA. E3 was the most soluble estrogen among the selected chemicals (Yamamoto et al. 2003) and the relatively high solubility made E3 tend to be transported into water phase and thus be degraded by microorganisms in activated sludge. It was also notable that E1 and E2 was not removed efficiently by biological processes due to the transformation of E2 into E1 and the deconjugation of their conjugates (glucuronides and sulfates) by bacteria in activated sludge (Belfroid et al. 1999; D’Ascenzo et al. 2003). Previous research showed that E1 was more persistent in biological processes than E2 (Ying et al. 2008). In present study, similar trend was found in oxidation ditches in STP-B. However, in STP-A, AAO process was found to remove larger amount of E1 than E2, which may be because that the microbial populations in the system were more efficient

Table 5 | Removal rates of EDCs in different unit operations

<table>
<thead>
<tr>
<th>Unit process</th>
<th>Data sets</th>
<th>Removal of EDC (%)</th>
<th>OP</th>
<th>BPA</th>
<th>EE2</th>
<th>E1</th>
<th>E2</th>
<th>17α-E2</th>
<th>E3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary aeration</td>
<td>A1 → A2</td>
<td>-1.1 to 14</td>
<td>1.7 to 21</td>
<td>-9.5 to 3.3</td>
<td>-30 to NA</td>
<td>-10 to 1.3</td>
<td>0.5 to 6.7</td>
<td>-24 to 1.1</td>
<td></td>
</tr>
<tr>
<td>Primary aeration</td>
<td>B1 → B2</td>
<td>-6.6 to 34</td>
<td>-5.8 to 31</td>
<td>-21 to 14</td>
<td>NA to 5.7</td>
<td>-23 to 12</td>
<td>NA to 1.3</td>
<td>-8.5 to 4.3</td>
<td></td>
</tr>
<tr>
<td>Primary sedimentation</td>
<td>C1 → C2</td>
<td>-14 to 0.4</td>
<td>-2.6 to 27</td>
<td>-19 to 24</td>
<td>27 to 51</td>
<td>-12 to 5.6</td>
<td>NA</td>
<td>-20 to NA</td>
<td></td>
</tr>
<tr>
<td>AAO</td>
<td>A2 → A3</td>
<td>29 to 78</td>
<td>82 to 91</td>
<td>62 to 100</td>
<td>52 to 66</td>
<td>13 to 32</td>
<td>NA to 23</td>
<td>83 to 100</td>
<td></td>
</tr>
<tr>
<td>Oxidation ditch</td>
<td>A4 → A5</td>
<td>25 to 67</td>
<td>82 to 84</td>
<td>64 to 94</td>
<td>10 to 22</td>
<td>-15 to 18</td>
<td>-10 to 5.8</td>
<td>81 to 100</td>
<td></td>
</tr>
<tr>
<td>Oxidation ditch</td>
<td>B3 → B4</td>
<td>21 to 55</td>
<td>64 to 87</td>
<td>54 to 77</td>
<td>34 to 51</td>
<td>42 to 74</td>
<td>-100</td>
<td>77 to 95</td>
<td></td>
</tr>
<tr>
<td>Oxidation ditch</td>
<td>B3 → B5</td>
<td>24 to 50</td>
<td>76 to 82</td>
<td>50 to 74</td>
<td>23 to 52</td>
<td>45 to 78</td>
<td>-100</td>
<td>63 to 92</td>
<td></td>
</tr>
</tbody>
</table>

*NA: not available, means the concentrations of influents and effluents in the unit are both lower than LOD.

†AAO: anaerobic–anoxic–oxic process.

‡'100' means influent concentration is lower than LOD and effluent is higher than LOD; '100' means that influent concentration is higher than LOD and effluent is lower than LOD.
in deconjugation (E2 formation) than in biodegradation (E2 decrease). Besides, removal of E1 and E2 in the oxidation ditch of STP-A was both lower than that in ditches of STP-B, which may depends on the operation parameters and influents quality.

CONCLUSIONS

An analytical method with SPE–GC–MS was developed for determining seven typical endocrine disrupting chemicals (EDCs) in sewage treatment plants (STPs). Among the seven selected EDCs, BPA and EE2 are two main types with rather high concentrations compared to that reported in other countries. E2 of high concentration in effluents of STPs can lead to high risk of reproductive problems to aquatic organisms in receiving water bodies. Relatively high removal efficiencies of E3, BPA and EE2 in biological processes are observed and moderate removal efficiencies of OP and E1 can be achieved as well. E2 can not be removed effectively in both biological and primary treatment processes of STP-A and STP-C, while oxidation ditches of STP-B can remove 42–78% of E2. Seasonal change of EDCs concentration between wet and dry season occurred in all three STPs.

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