

Behaviour of selected endocrine-disrupting chemicals in three sewage treatment plants of Beijing, China

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Abstract Occurrence and fate of eight kinds of selected endocrine-disrupting compounds (EDCs) in three sewage treatment plants (STPs) of Beijing, China was investigated. These EDCs, composed of 4-octylphenol (4-OP), 4-n-nonylphenol (4-n-NP), bisphenol A (BPA), estrone (E1), 17α -estradiol (17α -E2), 17β -estradiol (E2), estriol (E3) and 17α -ethinylestradiol (EE2), in every step of STPs, were simultaneously analysed by gas chromatography/mass spectrometry after derivatisation. All the EDCs were detected in the influents of three STPs, and BPA was the most abundant compound. The concentrations of

EDCs ranged from 36.6 ng/l of 17α -E2 (STP C) to 1342.3 ng/l of BPA (STP B) in the influent sewages and from below limits of detection of E2 and E3 (STP C) to 142.5 ng/l of E1 (STP B) in the effluent sewages. The STPs could not remove alkylphenols effectively from the aqueous phase with less than 40% reduction. BPA decreased over 90%, and steroid estrogens achieved considerable reductions from 64.8% of E2 to 94.9% of E3. Generally, biological treatment was more effective in removing alkylphenols, BPA and natural estrogens from the aqueous phase than primary treatment. However, the synthetic estrogen, EE2, was mostly removed by the primary treatment with about 63.5% reduction. It is the first time that the concentration of 17α -E2 in the sewage of China was reported in this paper. The compound might have a bearing with the waste effluents of dairy farms around urban area of Beijing.

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Introduction

There is an increasing concern on the potential harmful consequences of exposure to chemicals which are capable of modulating or disrupting endocrine system in recent years. These chemicals,

collectively known as endocrine-disrupting compounds (EDCs), are defined as exogenous agents that interfere with the production, release, transport, metabolism, binding, action or elimination of the natural hormones in the body responsible for the maintenance of homeostasis and the regulation of developmental processes (Kavlock 1999). They consist of a wide range of industrial and household chemicals such as polychlorinated biphenyls, chlorinated insecticides, alkylphenols and their ethoxylates, bisphenol A (BPA) and steroid estrogens. The environmental occurrence of EDCs may be implicated in the adverse health consequences, including the development of testicular and prostate cancer and reduced sperm production in humans and demasculation, feminisation, alteration of immune functions and decreased fertility in birds, fish and mammals (Mol et al. 2000).

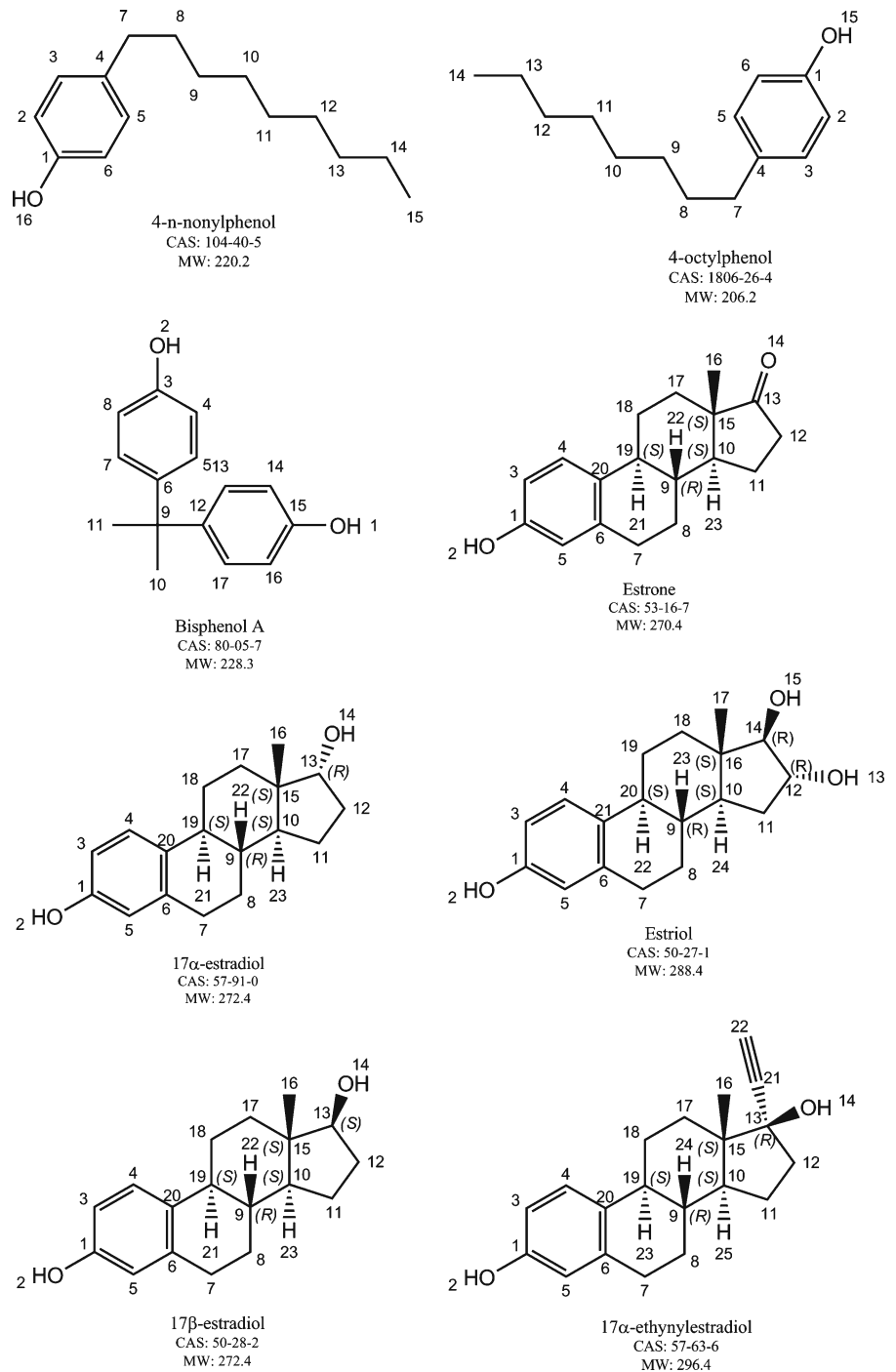
Gas chromatography–mass spectrometry (GC/MS) technique may be used to simultaneously measure EDCs such as phenolic compounds and steroid hormones in various environmental matrix (Beck et al. 2008; Sakamoto et al. 2006; Zhang et al. 2006). The most common silylation procedure to derivatise compounds bearing hydroxyl groups uses *N,O*-bis (trimethylsilyl) trifluoroacetamide (BSTFA) and *N*-(*tert*-butyldimethylsilyl)-*N*-methyltrifluoroacetamide (MTBSTFA), which leads to the formation of trimethylsilyl and *t*-butyldimethylsilyl derivatives, respectively. Although Shareef et al. (2006) reported that the two reagents for derivatising estrone (E1) and 17 α -ethinylestradiol (EE2) may result in the partial conversion of EE2 derivatives to their respective E1 derivatives, Zuo and Zhang (2005) and Shareef et al. (2006) found that BSTFA could give good results when the derivatisation was carried out in a pyridine solvent.

Extensive researches conducted outside of China (Andersen et al. 2003; Nakada et al. 2006; Sarmah et al. 2006; Servos et al. 2005) have shown that the present treatment processes of sewage treatment plants (STPs) could not remove EDCs completely, and some EDCs with nanograms per liter to micrograms per liter level of concentration were found in the effluent sewage. Desbrow et al. (1998) and Routledge et al. (1998) indicated that STP effluents with the presence of the natural

estrogens 17 β -estradiol (E2) and E1 as well as the synthetic estrogen, EE2, might be responsible for the estrogenic effect on fish in the receiving waters. Discharge of effluent sewage can be recognised to be the important source for EDCs to enter into the natural environment. In China, Jin et al. (2005) reported the concentrations of natural estrogens and xenoestrogens in the influent and effluent of a Wuhan STP. Estrogens (except EE2) in the influent were found with the concentrations of 6.5–8954.9 ng/l and estrogens [except EE2 and estriol (E3)] in the effluent with the concentration of 3.2–2473.5 ng/l. Besides, about 30 kinds of EDCs with the removal efficiency of 70–99% were detected in a Beijing STP (Du et al. 2004). So far, however, the relevant researches on EDCs in STPs of China were scattered, and only EDCs in the influent and effluent sewage were determined in most of the researches. Therefore, there is no comprehensive and profound survey on the occurrence and fate of EDCs in STPs of China at present.

In this paper, eight target compounds, consisting of three phenolic chemicals and five steroid estrogens (Fig. 1), were selected to be simultaneously determined by GC/MS in the each step of three STPs with different treatment processes in Beijing, China. These compounds studied were selected according to their physicochemical characteristics, the availability of analytical methods and the reference to the literatures for estrogenic information on the selected compounds (Khanal et al. 2006; Routledge and Sumpter 1996). Besides, one point should be noted that it is the first time, to the best of our knowledge, for 17 α -estradiol (17 α -E2) to be studied in STPs of China. It was reported that 17 α -E2 epimer was more prevalent in dairy cattle than its β -epimer (Hanselman et al. 2003). Beijing city has big production of fresh milk with more than ten dairy farms around urban areas. Therefore, identifying α -epimer may be helpful to better understand the distribution of EDCs in STPs in Beijing. The purpose of this work includes three points. The first is to elucidate the occurrence and fate of EDCs in STPs of Beijing, China on the whole. Secondly, the data of EDCs distribution in Beijing are expected to be helpful for establishing and enriching the database of EDCs in the sewage

Fig. 1 Target compounds selected in this study



of China. The last but not least, this study is expected to cause more concerns from institutions of China about the occurrence of EDCs in sewage and their environmental risk and consequently facilitate the relevant investigations carried out in China.

Methods and materials

Beijing sewage treatment plants

Three STPs of Beijing with different treatment processes were selected in this study (Fig. 2).

STP A has a planned treatment capacity of 400,000 m³/day. It consists of two stage projects, each of which has the capacity of 200,000 m³/day. The anoxic/anaerobic/oxic (called “inverse A/A/O”) and anaerobic/anoxic/oxic (called “A/A/O”) processes are introduced in the first stage and the second stage project, respectively. Phosphorous could be released to the aqueous phase in the anaerobic treatment step to some extent due to the effect of phosphorous-accumulating bacteria, and much more amount of phosphorous could subsequently be accumulated in the solid phase in the oxic treatment step by the bacteria, leading to the removal of phosphorous

from the aqueous phase. Denitrification could occur in the anoxic treatment step, which would cause the removal of nitrogen from the aqueous phase. Besides, chemical oxygen demand (COD) and biological oxygen demand (BOD) would be further decreased in the oxic treatment step in addition to the anaerobic and anoxic treatment steps. The reasons for the employment of the inverse A/A/O process may be that better removal of phosphorous are expected, as good anaerobic condition can be maintained in the process. The daily flow rate is about 350,000 m³. STP B, which has the biggest treatment capacity in China, up to 1,000,000 m³/day, serves a population of about

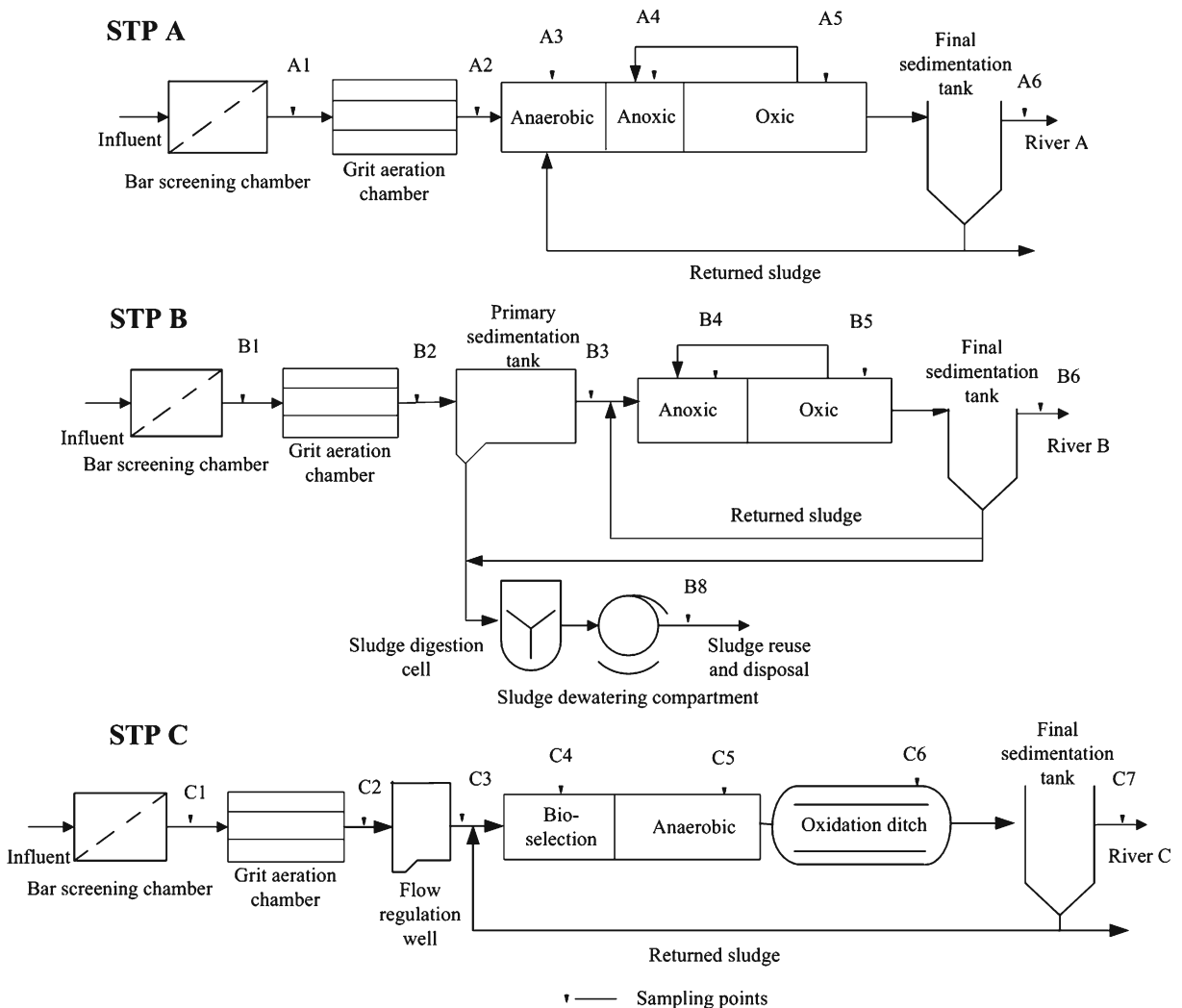


Fig. 2 Treatment processes adopted by three Beijing STPs studied and the location of sampling points

2,400,000. The main treatment process employed in the plant is anoxic/oxic (A/O). The daily flow rate is about 800,000 m³. STP C is capable of treating wastewater at 200,000 m³/day and serves a population of 400,000 within the scope of 86.0 km². The daily flow rate of the plant is about 180,000 m³. The process of extended aeration oxidation ditch (OD) with anaerobic reactor ahead is introduced in the plant. Meanwhile, a biological selection tank with one fiftieth effective volume of anaerobic reactor is placed in front of the reactor to refrain from growth of filamentous bacteria due to its high organic load. Thus, it can be helpful to alleviate and control the sludge bulking. More details of the three STPs are shown in Table 1. There are two reasons for selecting the three STPs. One is that they are three of the STPs with the largest treatment capacity in Beijing. More than 60% of sewage in the urban area of Beijing is treated by the three STPs. The other is that they represent the state of the art of STPs in Beijing as the treatment processes introduced are typical there.

Chemicals and reagents

The reference standards of 4-octylphenol (4-OP), 4-n-nonylphenol (4-n-NP), BPA and 17 α -E2 were purchased from Sigma-Aldrich, USA; E1, E2, E3 and EE2 were purchased from Wako, Japan. Internal standards, 17 β -estradiol 17 acetate (E2-17AC) and 17 β -estradiol-d2 (E2-d2) were supplied by Dr. Ehrenstorfer, Germany. All these standards were of high purity over 98% and stored at 4°C. Standards were dissolved in methanol to prepare the stock solutions and working solution. All these standard solutions were stored at -20°C in the dark. The derivatisation reaction reagent, BSTFA, with 1% trimethylchlorosilane (TMCS) was purchased from Sigma-Aldrich. All the solvents used were HPLC grade or higher. Methanol, acetone and dichloromethane were supplied by Fisher, USA, and methyl *tert*-butyl ether (MTBE) was purchased from Sigma-Aldrich. Ultrapure water was obtained with NANOPURE ultrapure water system from Barnstead/Thermolyne, USA.

Table 1 Main characteristics of three sewage treatment plants in Beijing

STP	Population (10 ⁴)	Flow rate (10 ⁴ m ³ /day)	Process	Retention time		COD (mg/l)		BOD ₅ (mg/l)		NH ₃ -N (mg/l)	
				Hydraulic (h)	Solid (d)	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.
A	81.4	35	Inverse A/A/O ^a (A/A/O) ^b	11.5	6–7	260.6	31.6	122.5	6.4	60.4	0.2
B	240.0	80	A/O	14.8	4–6	330.1	32.0	168.7	6.4	46.9	4.2
C	48.0	18	OD	17.4	16–17	262.0	32.9	130.6	6.3	63.2	0.5

A/O anoxic/oxic, OD oxidation ditch, *Inf.* influent, *Eff.* effluent

^aInverse A/A/O, anoxic/anaerobic/oxic. The process is introduced in the first project of STP A

^bA/A/O, anaerobic/anoxic/oxic. The process is introduced in the second project of STP A where the sampling points were located

Sampling and pretreatment

Two sampling campaigns were carried out, and samples were taken in the each step of the processes in the three STPs during each campaign. The first sampling campaign was conducted between May and July 2007 and the second one between October and December 2007. The effluent sewage from bar screening chamber was considered as the influent sewage in all of the three STPs. The sampling points in the three STPs are shown in Fig. 2. Unfortunately, effluent from the final sedimentation tank of STP C (the sampling point of C7) was not available during the second time sampling. Therefore, the performance of the process in STP C was judged mainly from the data obtained during the first sampling campaign. Four-litre samples taken at each point was put into amber glass bottles with Teflon liner caps, regulated pH to 3.0 by sulfuric acid, transported to laboratory and stored at 4°C immediately. The pretreatment of the samples was completed in 48 h. One-litre sample, added 100 ng surrogate, E2-d2, was pre-filtered with a GF/B (1 µm) glass fiber filter (Whatmans, USA). The sample, subsequently, was introduced to an Oasis HLB cartridge (6 cc/200 mg, Waters, USA) on a vacuum 20-position extraction manifold (Waters) to extract the analytes. Before solid phase extraction, the cartridge was conditioned with MTBE and then rinsed by methanol followed by ultrapure water for equilibration. The extraction was done at a flow rate less than 5 ml/min. The cartridge was eluted with 10 ml dichloromethane/acetone (7:3), and the extract was cleaned up by a silica gel cartridge. After cleanup, the extract was evaporated to dryness under a gentle nitrogen stream following the addition of 100 ng E2-17AC as internal standard. Then, the dry residue was derivatised by adding 50 µl pyridine and 100 µl BSTFA (with 1% TMCS). The derivative was further dried, and the residue was redissolved in 100 µl *n*-hexane for GC/MS analysis.

GC/MS analysis

Analysis and quantification of the analytes were performed using a GC/MS system (DSQ, Thermo Electron Co., USA) equipped with a gas chro-

matograph (Trace GC Ultra) interfaced with a tandem quadrupole mass spectrometer (DSQ). The analytes were separated by a VF-5 capillary column (30 m × 0.25 mm i.d. × 0.25-µm film thickness). The parameters for GC described by Zhang et al. (2006) were adopted with minor modification. In brief, they were set as follows. Sample injection was 1 µl in a splitless mode. Helium was used as the carrier gas at a constant flow rate of 1 ml/min. The inlet temperature of injector was 250°C. The temperature program for GC column was first run from 100°C (equilibrium for 1 min) to 200°C at 10°C/min, then from 200°C to 260°C at 15°C/min, from 260°C to 300°C at 3/min and at last maintained at 300°C for 4 min. The MS was by electron ionisation and run in TIC mode from *m/z* 50 to 600 for qualitative analysis or selected ion monitoring mode for quantitative analysis. The inlet and MS transfer line temperature were kept at 280°C, and the ion source temperature was at 250°C. Quantification of real samples was performed by comparison of integration of selected ion chromatograms of target compounds with that of internal standard, E2-17AC. A linearity regression function was set up based on calibration measurement with concentrations between 10 µg/l and 10 mg/l (eight points). There was a good linearity in the detected range, and correlation coefficients (R^2) were 0.9945 for 4-OP, 0.9968 for 4-*n*-NP, 0.9983 for BPA, 0.9974 for E1, 0.9968 for 17 α -E2, 0.9961 for E2, 0.9991 for EE2 and 0.9984 for E3. In every batch of measurements, the GC/MS system was calibrated with standard compounds in a linear range of 10 µg/l–10 mg/l. Measurement results were recalculated regarding recovery of the surrogate, E2-d2. Table 2 shows some main parameters for target compounds analysed by GC/MS. The obtained method limit of detection (LOD) ranged from 0.3 ng/l (E3) to 13.8 ng/l (BPA), and the limit of quantification (LOQ) varied between 0.9 ng/l (E3) and 46.1 ng/l (BPA). The recoveries of target compounds in sewage, corrected by that of E2-d2, were above 65%, indicating acceptable precision of the present procedure. In addition, spiked matrices (not less than 50% of the number of samples) including STP influent and effluent sewages were treated and analysed to determine the recoveries during the measurements of every batch of samples in order to assure the precision

Table 2 Typical parameters for selected EDCs analysed by GC/MS

Target compound	Retention time (min)	<i>m/z</i> for quantification	<i>m/z</i> for qualification	LOD (ng/l)	LOQ (ng/l)	Recovery in pure water (%)	Recovery in sewage (%)
4-OP	13.05	278	179	1.2	3.8	78.2–83.7	83.4–90.4
4- <i>n</i> -NP	14.09	292	–	0.6	1.9	68.1–85.8	71.4–97.9
BPA	16.78	357	372	13.8	46.1	85.8–111.9	85.1–115.8
E1	20.76	342	218,257	1.5	4.9	91.7–105.2	74.4–76.6
17 α -E2	20.32	416	286,326	0.4	1.3	95.0–96.3	69.6–76.4
E2	20.63	416	286,326	0.6	2.1	92.0–95.5	75.4–86.0
EE2	21.51	425	285,440	0.4	1.5	71.2–91.3	68.0–85.6
E3	21.99	504	312,387,415	0.3	0.9	89.5–94.0	65.2–89.2

of quantification. Procedure blanks and solvent blanks were also treated and analysed alongside the measurements.

Results and discussion

Occurrence of selected EDCs in the influents

All the selected EDCs were found in the influent sewages of the three STPs, and BPA was the most abundant compound with a mean concentration of 933.2 ng/l (Table 3). The maximum concentration of BPA was observed in STP B with a value of 1416.7 ng/l in the first sampling campaign. The concentrations were comparable with those found in STPs of England (960.2 ng/l; Hernando et al. 2004), but higher than those found in STPs of Japan (345.0 ng/l; Nakada et al. 2006) and Italy (334.0 ng/l; Lagana et al. 2004).

The two alkylphenols, 4-OP and 4-*n*-NP, were detected in the influents with mean concentrations of 92.2 and 85.8 ng/l, respectively. In the previous studies, lower concentrations of 4-OP (44.3 ng/l) and 4-*n*-NP (33.3 ng/l) were reported in STPs in England (Hernando et al. 2004) and Greece (Gatidou et al. 2007).

In the case of natural estrogens, the mean concentrations were 368.9 ng/l for E1, 85.2 ng/l for 17 α -E2, 63.1 ng/l for E2 and 224.5 ng/l for E3. Among the natural estrogens, E1 and E3 were most abundant in the influents of the three STPs, which was consistent with the finding reported by Korner et al. (2000). It may result from the fact that E1 and E3 are the major excretion products of steroid estrogens from human and wildlife (Ying et al. 2002a, b). Besides, the presence of natural estrogens in the influents might be partially concerned with dairy farms around urban areas of Beijing mentioned above. A previous study showed that dairy waste effluents could be a source of natural estrogens in the environment (Sarmah et al. 2006). Besides, Erb et al. (1977) reported that more than 90% estrogens excreted by cattle (*Bos taurus*) were free 17 α -E2, E2 and E1 as well as their respective conjugates. The concentrations of E2 were comparable with those detected in STPs in England (78.1 ng/l; Hernando et al. 2004). However, the concentrations for all the

Table 3 Distribution of EDCs (ng/l) along the three Beijing STPs in two sampling campaigns

STP	Sampling point	4-OP	4-n-NP	BPA	E1	17 α -E2	E2	E3	EE2
A	A1	159.9 (110.9)	101.3 (91.5)	699.9 (783.9)	911.5 (544.9)	90.9 (135.6)	131.0 (77.4)	505.5 (332.1)	243.1 (222.5)
	A2	165.4 (118.0)	86.2 (77.2)	800.4 (956.5)	747.2 (480.3)	85.7 (141.5)	104.6 (62.7)	448.2 (316.1)	82.6 (116.3)
	A3	132.4 (85.2)	71.9 (54.2)	120.7 (315.1)	403.9 (248.9)	77.9 (42.1)	145.9 (78.6)	173.8 (97.8)	71.3 (66.6)
	A4	102.3 (62.4)	59.4 (38.7)	129.1 (164.0)	223.5 (137.4)	60.9 (32.3)	172.2 (92.5)	87.3 (45.5)	79.9 (51.1)
	A5	108.5 (64.3)	72.1 (45.3)	107.2 (122.3)	138.8 (90.2)	n.d. (1.1)	98.1 (53.5)	18.2 (10.1)	64.9 (39.8)
	A6	95.7 (54.5)	51.7 (30.8)	60.6 (98.6)	181.2 (104.4)	49.4 (25.3)	47.7 (27.4)	n.d. (3.0)	87.4 (60.7)
B	B1	114.4 (120.5)	68.7 (100.6)	1416.7 (1342.3)	775.4 (445.8)	119.6 (83.5)	87.5 (58.9)	464.4 (239.3)	175.6 (238.4)
	B2	135.6 (125.3)	62.5 (136.8)	1965.6 (2277.1)	753.0 (429.0)	79.4 (65.5)	78.9 (43.6)	441.7 (223.8)	122.3 (140.9)
	B3	101.4 (105.0)	64.9 (95.0)	1588.7 (2495.1)	749.7 (427.9)	69.5 (64.3)	69.1 (38.3)	250.9 (134.1)	81.7 (91.6)
	B4	118.9 (74.2)	59.8 (49.4)	679.8 (486.1)	209.9 (138.0)	300.9 (155.9)	88.9 (46.0)	194.1 (107.9)	119.0 (63.2)
	B5	91.6 (91.8)	58.6 (105.0)	234.1 (148.85)	171.5 (100.6)	173.8 (90.8)	54.9 (27.8)	71.2 (40.5)	70.1 (35.9)
	B6	103.7 (93.7)	58.7 (86.9)	138.4 (88.7)	253.8 (142.5)	144.2 (75.0)	64.3 (33.2)	61.3 (33.0)	112.4 (55.2)
C	C1	38.5 (45.0)	43.9 (65.1)	806.3 (673.5)	132.0 (116.1)	22.4 (36.6)	31.7 (53.0)	134.9 (102.0)	873.8 (622.9)
	C2	50.6 (47.0)	56.7 (63.6)	917.6 (632.5)	114.1 (159.2)	12.6 (30.9)	21.9 (25.8)	119.2 (111.3)	127.5 (156.1)
	C3	36.7 (35.1)	44.4 (73.2)	787.1 (641.8)	114.0 (142.3)	15.8 (29.7)	30.0 (23.4)	133.5 (82.2)	163.1 (220.9)
	C4	21.7 (32.2)	35.8 (55.5)	383.7 (261.4)	26.1 (48.8)	9.7 (13.6)	15.4 (16.7)	49.5 (107.9)	26.1 (26.8)
	C5	12.2 (19.1)	20.8 (34.6)	203.4 (159.6)	10.2 (30.6)	3.8 (7.6)	6.3 (10.3)	27.3 (64.0)	44.4 (29.0)
	C6	14.3 (26.4)	15.5 (23.4)	127.1 (130.9)	10.9 (17.2)	1.3 (6.7)	2.5 (6.6)	9.2 (16.8)	63.0 (39.9)
	C7	10.8	15.5	56.9	1.2	n.d.	n.d.	n.d.	n.d.

Data from the first sampling campaigns are presented before the parentheses and the mean values from two sampling campaigns inside the parentheses. All the results below LODs are treated as the values of LODs

natural estrogens except 17 α -E2 on the whole were higher than those found in STPs in other regions, e.g. Germany (E1, 27.0 ng/l; E2, 15.0 ng/l; Ternes et al. 1999), Italy (E1, 35.0 ng/l; E2, 25.0 ng/l; E3, 31.0 ng/l; Lagana et al. 2004) and Japan (E1, 117.0 ng/l; E2, 19.3 ng/l; E3, 133.5 ng/l; Nakada et al. 2006). No comparable data for 17 α -E2 in the influent sewage is found at present; nevertheless, the maximum concentration, up to 74 ng/l, was reported in the streams in the USA (Kolpin et al. 2002).

For synthetic estrogen, EE2, the mean concentration in the influents was 187.9 ng/l, higher than that found in Italy (average = 3.0 ng/l, maximum = 13.0 ng/l; Baronti et al. 2000) and in France (average = 4.9–7.1 ng/l; Cargouet et al. 2004). The higher concentration might be partially due to both large population in Beijing (over 17 million people) and birth control policy which leads to wide usage of EE2-based oral contraception pills in women.

Behavior of selected EDCs along the STPs

The concentrations of target compounds in every step of the processes are presented in Table 3. Since the STPs studied were all introduced activated sludge treatment processes, the processes on the whole could be divided into two parts: the primary/physical treatment (including aerated grit chamber, primary sedimentation tank and flow-regulating well) and the secondary/biological treatment (including anaerobic reactor, anoxic reactor, aerated reactor, biological selection tank, OD, final sedimentation tank, etc.). Figure 3 describes the performances of the two parts of the three STPs on removing EDCs from the aqueous phase. The removal efficiencies of all selected EDCs were calculated taking into account the measured concentrations at the inlet of the plants, the inlet of biological treatment steps and the final effluents.

Alkylphenols

In the case of two alkylphenols, their average removal efficiencies were less than 10% by the primary treatment and about 45% by the biological treatment. Therefore, they could not be

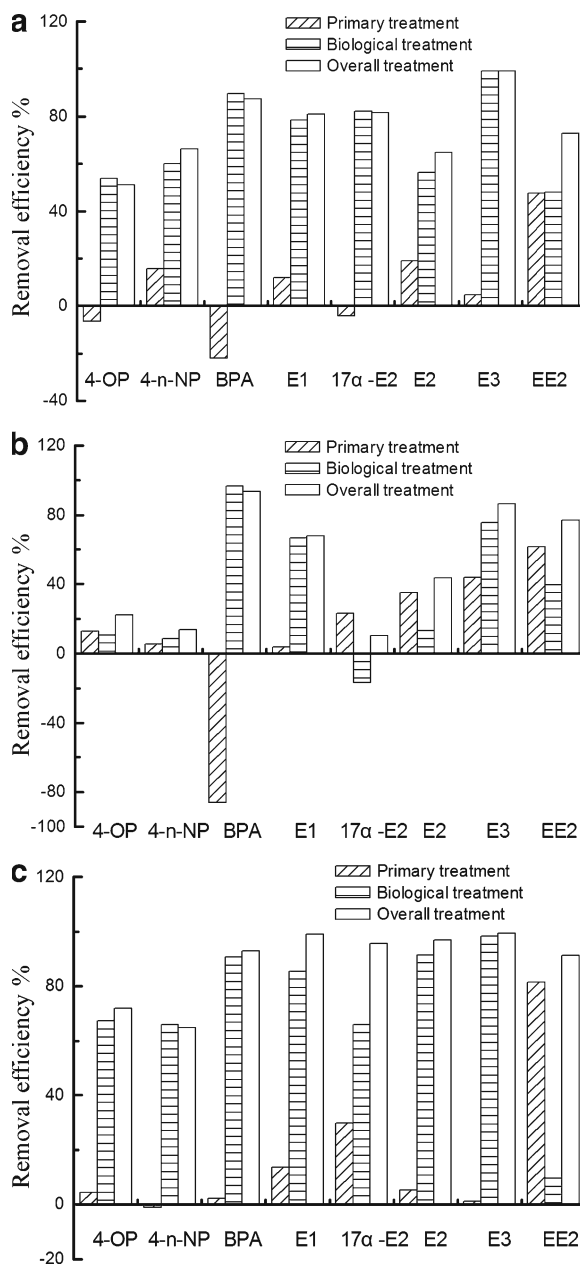


Fig. 3 Removal of selected eight EDCs in the primary and biological treatment of **a** STP A, **b** STP B and **c** STP C in Beijing

effectively reduced in STPs on the whole. Based on their removal in STPs A and C, the biological treatment may be relatively more effective to remove them compared with the primary treatment. During the primary treatment, their concentrations in sewages even increased after through

aerated grit chamber. For example, the concentrations of 4-OP would be 3.0–35% higher. That might be due to the biodegradation of AP_nEOs in the chamber. The long-chain AP_nEOs would be shortened and further be degraded into APs. On the other hand, adsorption of APs to particles would reduce their contents in sewage because of their relatively high hydrophobic property (Ying et al. 2002a, b). Consequently, concentrations of APs decreased slowly and sometimes even increased a little during the physical treatment. As mentioned above, they got poorest removal efficiency in STP B. That might be derived from the difference among the processes introduced in the three STPs. STP B employed conventional activated sludge process, in front of which an anoxic tank was added in order to improve the function of denitrification of the whole system. In the other two STPs were introduced innovative activated sludge process, i.e. STP C employed OD where an anaerobic tank was pre-located and STP A utilised the process of A2/O. Anaerobic sludge has an ability of degrading APs (Hesselsoe et al. 2000). It also can be seen from Table 3 that concentrations of APs decreased about 20% after the treatment of anaerobic tank. Therefore, overall removal efficiency of EDCs was also enlarged. In addition, the removal efficiency of APs during the biological treatment in STP C was highest among the three STPs. The reason for it might partially be that their concentrations in the influent were lowest among the influents of the three STPs, and their adsorption to sludge would account for a considerable part of their removal.

The mean concentrations in the effluents were 53.0 ng/l for 4-OP and 44.4 ng/l for 4-*n*-NP. Lower or comparable concentrations were found in England for 4-OP (17.6 ng/l; Hernando et al. 2004) and in Greece for 4-*n*-NP (43.3 ng/l; Gatidou et al. 2007). On the whole, the two alkylphenols got relatively poor reduction in the three STPs, especially in STP B, as the removal efficiency of 4-*n*-NP was only 13.6% and 4-OP 22.2%. The average removal efficiency of APs was less than 40%.

Bisphenol A

As for BPA, it was nearly not removed during the primary treatment. Its concentration in the

sewage after the primary treatment even became much higher than before in STP B. However, BPA could be removed by over 90% during the biological treatment. According to its relatively lower hydrophobic nature, its removal might not result from adsorption to activated sludge, but from biodegradation. The three different biological treatment processes could achieve good removal efficiency of BPA, which was equivalent to that obtained in five STPs of Tokyo, Japan reported by Nakada et al. (2006). All the plants used primary and secondary treatment with activated sludge process.

The mean concentration in the effluents was 81.4 ng/l, comparable with those found in Japan (56.2 ng/l; Nakada et al. 2006), in Italy (32.0 ng/l; Lagana et al. 2004) and in Germany (160.0 ng/l; Korner et al. 2000). Three STPs showed good capability of removing BPA with about 90% of overall reduction.

Steroid estrogens

The average overall removal efficiency of E1 was about 82.7%, of which the biological treatment accounted for 76.8% and primary treatment for 9.8%. For E2, the average overall removal efficiency was about 68.4%, of which 19.8% removal efficiency was obtained from the primary treatment as well as 53.7% from the biological treatment. E3 had 94.9% of the average overall removal efficiency, as the primary treatment contributed to 16.5% and the biological treatment 90.9%. On the whole, the biological treatment played a key role in the removal of these natural estrogens. The biological treatments in STPs A and C could achieve over 98% of E3 removal efficiency and about 70% of E2 removal efficiency. However, they were removed more effectively by the primary treatment than the biological treatment in STP B. That might be concerned with the primary sedimentation tank in this plant, which made the primary treatment more complicated. As there existed microorganisms in the primary sedimentation tank, E2 and E3 could partly be biodegraded, which would enhance the removal efficiency from the primary treatment in turn. On the other hand, E1 was the major biodegradation product of E2. Thus, E1 removal efficiency by the

primary treatment in STP B was lowest among the three STPs. In addition, it can be seen from Table 3 that E2 concentration in sewage increases a bit at the start of the biological treatment and then decreases. As E2 from human and wildlife are largely excreted as inactive glucuronide or sulfonide conjugates, these E2 conjugates would partly enter into the biological treatment units and be cleaved into E2 by the bacteria with common β -glucuronidase enzyme (Johnson and Sumpter 2001), which led to the increase on E2 concentration. Then, E2 concentration would be declined by the biodegradation. From the data achieved in the first sampling campaign, it could be seen that 17α -E2 could be effectively removed in STP C, and it was even lower than method LOD. It could also be removed to some extent in STP A. However, its concentration after the biological treatment was higher than that of the original influent in STP B. As can be seen from Table 3, the increase on its concentration is mainly caused by an anaerobic tank. The concentration decreased a bit after an aerobic treatment. Further study on the mechanism of 17α -E2 removal by the biological treatment should be needed.

The mean concentrations in the effluents were 82.7 ng/l for E1, 33.8 ng/l for 17α -E2, 20.5 ng/l for E2 and 12.3 ng/l for E3. Those concentrations were comparable with or higher than those reported by Sarmah et al. (2006) (E1, 84.7 ng/l; 17α -E2, 9.5 ng/l and E2, 14.8 ng/l) and Baronti et al. (2000) (E1, 18.4 ng/l; E2, 1.4 ng/l and E3, 3.0 ng/l). The removal efficiencies of E1 in this study were similar to those reported in Japan (86%; Nakada et al. 2006) and Brazil (83%; Ternes 1998) and higher than those reported in Germany (Ternes 1998). As for E3, its removal efficiencies were close to those reported in Japan (\sim 100%; Nakada et al. 2006) and in Italy (95.7%; Baronti et al. 2000). In the case of E2, they were lower than those reported in Canada ($>$ 75%; Servos et al. 2005) and Brazil ($>$ 92%), but slightly higher than those reported in Germany (Ternes 1998).

As for the synthetic estrogen, EE2, average overall removal efficiency was about 80.2%. The primary treatment accounted for 63.5% reduction, indicating more effectivity in removing the compound from the aqueous phase than the bi-

ological treatment with 32.4% reduction. That might have a bearing on the physicochemical properties of EE2. As k_{ow} of the compound was 4.15, showing highly hydrophobic nature than that of the natural estrogens (Sarmah et al. 2006), it could be more effectively removed from aqueous phase by sorption. Besides, Ternes et al. (1999) found that EE2 was biodegraded much more slowly, even though 40% was mineralised in 24 h in batch experiments. The mean concentration in the effluents was 64.6 ng/l, much higher than those in the USA (0.25 ng/l; Boyd et al. 2003), in Italy (0.54 ng/l; Baronti et al. 2000) and in Germany (1.0 ng/l; Ternes et al. 1999). As far as the overall removal efficiencies were concerned, they were comparable to those reported in Brazil (78%; Servos et al. 2005) and in Italy (85.0%; Baronti et al. 2000).

Variations between two sampling campaigns

As for individual target compound in every STP, it also showed different concentrations in the influents/effluent and behaviour along the processes during the two sampling campaigns (Table 3). For example, E2 was 131.0 ng/l in the influent and 47.7 ng/l in the effluent in STP A in the first sampling campaign. The overall removal efficiency obtained was 63.6%, of which 20.2% was from the primary treatment and 54.4% from the biological treatment in the campaign. In contrast, E2 was 23.9 and 7.0 ng/l in the influent and effluent, respectively, in the second sampling campaign. A 12.8% reduction by the primary treatment and a 66.3% reduction by the biological treatment were achieved, and the overall removal efficiency was 70.6%. The total concentrations of selected compounds were 3,222.3 and 936.9 ng/l, respectively, in influent and effluent sewages in STP B during the first sampling campaign, whilst those were correspondingly 2,036.4 and 242.6 ng/l with higher removal efficiency during the second sampling campaign. On the whole, the data appeared to show that better removal of selected EDCs and lower discharge of the compounds could be achieved during the second sampling campaign. In previous researches, Vieno et al. (2005) and Yang and Metcalfe (2006) reported the seasonal variations in the influent and effluent

concentrations of target compounds such as pharmaceuticals and musk fragrances in STPs and higher concentrations obtained in colder sampling times. However, similar variation trend could not occur in this study, as the first sampling campaign was in the summer and the second sampling campaign belonged to the winter of Beijing. For individual compounds selected, some exhibited higher concentration in colder sampling time for one STP, whilst they were present in lower concentration for another STP such as 4-*n*-NP. Analysis deviation (no more than 20%) could not account for this big difference. Therefore, it was difficult to say their correlation of variation in the influent and effluent concentrations with the season. More data from long-term monitoring are required to do this analysis exactly.

Discussion on the removal in the STPs

From the perspective of STPs studied, considerable variations among them were present in removing the selected individual EDCs. The difference may be due to various factors such as the water quality of influents, plant configurations, hydraulic retention time (HRT; Johnson et al. 2005) and solids retention time (SRT; Servos et al. 2005).

The type of the treatment process employed can be the primary factor, which has a great influence on the removal efficiency for EDCs in STPs. The STPs in this study all employed secondary treatment processes: anaerobic/anoxic/oxic process for STP A, anoxic/oxic process for STP B and oxidation ditch process for STP C. The overall removal efficiencies for individual EDCs except BPA varied from one STP to another. Typically, 17 α -E2 concentrations in the effluent surpassed that in the influent in STP B, whilst achieved about 41.9% and 95.5% of removal efficiencies in STP A and STP C, respectively, in the first sampling campaign. Previously, oxidation ditch was found to result in the highest elimination of biodegradable pharmaceuticals (Kanda et al. 2003). Removal of EDCs in STP C seemed to support the finding as the target compounds were furthest reduced in the plant. For example, the overall removal efficiency for target compounds altogether was 92.1% in

STP C during the first sampling campaign, higher than that in STP A (79.8%) and in STP B (70.9%).

The input of EDCs and their metabolites into STPs could be highly variable and possibly control some of the variability observed in the concentration of targeted compounds. The input into a STP would be affected by a number of factors, for example population served by the STP (Castiglioni et al. 2006), composition of wastewater, the presence of chemical-industry factories, life style and even dilution by heavy rain (Tauxe-Wuersch et al. 2005). In this study, the total influent concentrations of EDCs during two sampling campaigns were most abundant in STP B where half of the input was composed of industrial wastewater.

SRT and HRT are two important design parameters and may be considered as key factors to evaluate the removal efficiencies of the compounds in the STPs. Longer HRT or SRT were observed to facilitate better removal of EDCs in STPs in previous studies (Johnson et al. 2005; Servos et al. 2005). This might occur due to the increased contact time of EDCs and the microorganisms with longer HRT or the enrichment of certain microbial communities which excrete enzymes able to break down EDCs with longer SRT. SRTs for the three STPs of Beijing were 6–7, 4–6 and 16 days for STPs A, B, and C, respectively. In the same sequence, HRTs were 7.7, 10.3 and 14 h, respectively. The overall removal efficiencies of EDCs were biggest in STP C, median in STP A and smallest in STP B. It seemed that longer SRT would lead to better removal of EDCs in STPs. However, the current study used a limited number of samples in only three different plants with different treatment process characteristics, which would affect the strength of any underlying relationships. Therefore, no statistical correlations between EDCs and SRT or HRT were obtained in this study. Additional controlled studies are required to more fully investigate these relationships, especially the potential relationship between SRT and the removal of EDCs.

Conclusions

This study showed that the selected EDCs were ubiquitous in the influent and effluent sewages

in three STPs of Beijing and therefore could not be completely removed by the present treatment processes. Concentrations of these compounds in the effluent sewages were comparable with or higher than those found in other countries, indicating that more attention should be paid to the environmental risk caused by discharge of EDCs in this region in the future. On the whole, the biological treatment could remove more effectively alkylphenols, BPA and natural estrogens from aqueous phase than the primary treatment. In contrast, the synthetic estrogen, EE2, could be reduced more effectively by the primary treatment due to its highly hydrophobic nature and slow biodegradation. Besides, the removal efficiencies of each compound varied from one STP to the next. It could not be attributed to longer HRT or SRT because of diverse characteristics of STPs and limited data set. In addition, variations in the influent and effluent sewages for every target compound occurred between the two sampling campaigns in different seasons. More data from long-term monitoring are needed to correlate the variations with seasonal change.

It is the first time that the concentration of 17 α -E2 in the sewage of China was reported. The compound is supposed to originate from the waste effluents of dairy farms around the urban area of Beijing. In consequence, the analysis of the compound may be helpful to better understand the occurrence of EDCs in the region.

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