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Fate of Estrogens Wastewater Treatment Plants in Korea

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Abstract. The aim of this study was to investigate the fate of the three most common natural estrogen in municipal wastewater treatment plants (WWTPs). We measured Estrogens in the samples taken from municipal wastewater treatment plants (WWTPs) in Korea to understand their occurrence concentrations and to survey their fate of natural estrogen in WWTPs. The samples were collected three times and all samples were collected in glass bottles. Analysis of free estrogens was used solid-phase extraction with LC/MS/MS. As a this study result, estriol(E3) was detected at higher concentrations than other Estrogens. Concentration of estriol(E3) was 81.7ng/L in effluent. The sewage treatment completely removed residues of estrogen and with good efficiency. 17β-estradiol (E2) and estriol(E3) was almost eliminated in effluent. The removal rate of estrone (E1) was 90~93, 80~84, 82~86 and 78~82% respectively for A, B, C and D STP.

Keywords : Estrogen, WWTP, LC/MS/MS detection etc.

1. Introduction

The issue of Estrogens has been an issue of global concern for over a decade (Sumpter and Johnson, 2008). The human population and associated wastewater treatment plants (WWTPs) are considered to be the major source of these chemicals in the aquatic environment (Harries et al., 2000). Also, major source is believed incomplete removal in sewage treatment plants (STPs) followed by discharge in the effluent (Johnson et al., 2000; Tanaka et al., 2003). Most of the steroid estrogens of concern are of natural origin, particularly 17β-estradiol(E2), and its main metabolites estriol(E3) and estrone(E1). These are largely excreted from the body as sulphate and glucuronide conjugates through urine (Jonson and Williams, 2004). Few studies on the fate of these compounds in wastewater treatment process have been reported due to their low and the associated difficulty in analysis (Kim et al., 2006). Therefore, in this study, the occurrence of natural estrogens in four municipal WWTPs were investigated to comparing their concentrations and to grasp their behaviors.

2. Material and Methods

2.1. Sampling

Targeted 3 compounds were shown in Table 2. A sampling in Korean WWTPs was planned total three times, depending on the season in 2011 to 2012. Four WWTPs were conducted two time of August, 2011 and January, 2012. All samples were collected in glass bottles. The sample bottles were first rinsed twice with the sample water before 1000 mL was collected. Extraction volumes were 1000mL, for sewage influent, primary effluent or secondary effluent, respectively. The bottles were stored in cooling box during their transport back to our laboratory.

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2.2. Sample Pretreatment

Samples were filtrated through the glass fiber filter (Whatman GF/B, 1 μm pore-size). After filtration, all samples acidified pH adjustment with 20% acetic acid and solid phase extraction (SPE) with Oasis HLB (Waters, 200mg, 6cc) cartridges was carried out at a flow rate of 10 mL/min. Then the cartridge was carried to Japan. The cartridge was dried and eluted with mainly methanol. Both final elutes were further evaporated to dryness under gentle nitrogen stream. The residue was immediately dissolved 1mL of acetonitrile and Milli Q (1:9) solution. Finally, 10μL were injected into the UPLC/MS/MS system under the developed method.

2.3. LC-MS/MS Analysis

The Estrogens were eluted from the cartridge using methanol. Methanol was eluted through the cartridge to release the free estrogens followed by the by NH_4OH in Methanol to elute the conjugated estrogens into a separate fraction. Both final elutes were further evaporated to dryness under gentle nitrogen stream. The residue was immediately dissolved in 1mL of acetonitrile and Milli Q (1:9) solution. Finally, 10 $\mu\ell$ were injected into the UPLC/MS/MS system under the developed method (Vimal Kumar et al., 2009). UPLC(ACQUITY UPLCTM system, Waters) was used for liquid chromatographic separations. ACQUITY UPLC 1.7μm Bridged Ethyl Hybrid (BEH) particle size columns (130Å pore size, with hybrid particle end-capped substrate) were used in this study. Reduction in column particle size (1.7μm) could provide improved peak resolution and high pressure with high liner velocity of the gradient (Wren and Tchelitcheff, 2006).

Table 1: Information of the survey WWTPs

WWTP	Operation capacity(m^3/day)	HRT (h)	Treatment processes and sampling points(n)
N	1,000,000	6.1	Inf(1) → CAS → NaOCl → Eff(2)
T	1,100,000	5.4	Inf(1) → CAS → NaOCl → Eff(2)
S	2,000,000	6.2	Inf(1) → CAS → Cl → Eff(2)
Y	48,000	6 - 8	Inf(1) → B3 → Cl → Eff(2)

HRT: hydraulic retention time, Inf: Influent, A2O: anaerobic/anoxic/oxic process, CAS: conventional activated sludge, B3: bio best bacillus, Eff: effluent, NaOCl: sodium hypochlorite disinfection, Cl: Chlorination

3. Results and Conclusions

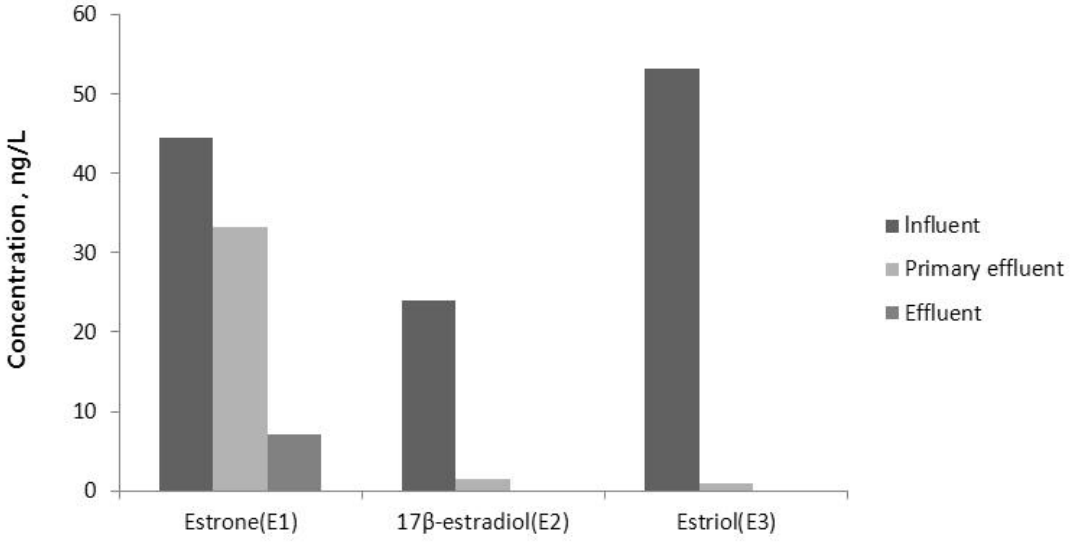
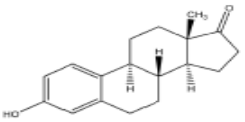
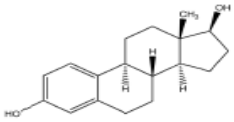
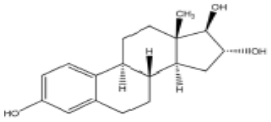


Fig. 1: Average concentration of WWTPs in Korea

As a this study result, estriol(E3) was detected at higher concentrations than other Estrogens. Concentrations of estriol(E3) was 81.7ng/L in effluent. The sewage treatment completely removed residues of estrogen and with good efficiency. 17β-estradiol (E2) and estriol(E3) was completely eliminated in effluent. The removal rate of estrone (E1) was 93, 84, 86 and 81% respectively for four wastewater treatment plants (WWTPs) in korea. According of report, Concentration of estrone in British WWTPs effluent was 1.4~76ng/L. Japan was 2.5~34ng/L, Canada and ltaly was 3ng/L. In this study, Average concentration of estrone in Korea WWTPs effluent was 0~7.15ng/L. It was higher than concentration of Canada and Italy. Also, Concentration of 17β-estradiol in British WWTPs effluent was 2.7~48ng/L. Japan was 0.3~2.5ng/L, Canada was 6ng/L.

Table 2: Characteristic of estrogen

Free estrogens	Used abbreviation	Molecular formula	Molecular weight	Structure of the free estrogen
Estrone	E1	$C_{18}H_{22}O_2$	270.4	 Estrone (E1) $C_{18}H_{22}O_2$ (MW 270.4)
17β-estradiol	E2	$C_{18}H_{24}O_2$	272.4	 17β-Estradiol (E2) $C_{18}H_{24}O_2$ (MW 272.4)
Estriol	E3	$C_{18}H_{24}O_3$	288.4	 Estriol (E3) $C_{18}H_{24}O_3$ (MW 288.4)

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