OCCURRENCE AND BEHAVIOR OF ESTROGENS IN WASTEWATER FROM HOUSEHOLDS, LIVESTOCK FARMS, HOSPITALS AND PHARMACEUTICAL MANUFACTURES IN KOREA

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Abstract

Estrogens with high potential of endocrine disrupting on aquatic organisms are discharged into the water system from various sources such as households, livestock farms, hospitals and pharmaceutical manufactures. We measured 4 natural and synthetic estrogens in wastewater samples from sewage treatment plants (STPs), livestock wastewater treatment plants (L-WWTPs), hospital WWTPs (H-WWTPs) and pharmaceutical manufacture WWTPs (P-WWTPs) in Korea. The concentrations and detection frequencies of estrone and estriol were higher than those of other target compounds. Among target STPs and WWTPs, L-WWTPs showed the highest concentrations of estrogens in the influents, and H/P-WWTPs had lower levels and detection frequencies of estrogens than those in STPs and L-WWTPs. Estriol showed satisfactory removal efficiencies (over 80%) in most of cases regardless of WWTP types, while estrone had wider range of the removal rates than estriol. 17α-Estradiol and 17β-estradiol were detected in most of L-WWTPs, and they were removed by over 90% except for 1 case. Overall, except for estrone, target estrogens have significant removal efficiencies (>80%) in the WWTPs.

Introduction

Estrogens, a group of steroid hormones, are emerging pollutants with high potential of endocrine disrupting on organisms in the aquatic ecosystem[1,2]. For example, these substances in the environment have caused induction of plasma vitellogenin and intersex in fish[3,4]. Most of emerging pollutants such as pharmaceuticals, synthetic musk fragrances and perfluorinated compounds are generated from anthropogenic sources, but estrogens have both natural and synthetic sources[3,4]. Natural estrogens (e.g., estrone, 17β-estradiol and estriol) are produced in humans and animals, and synthetic compounds (e.g., 17α-ethynilestradiol) are used in medicine (e.g., birth-control drugs)[2,5].

Wastewater is regarded as the most important source of emerging contaminants in the water environment. Especially, sewage and livestock wastewater are major pathways of estrogens in the aquatic environment[2]. Recently, hospitals and pharmaceutical manufactures, as well as STPs and L-WWTPs, have been considered as sources of estrogens in the water system[7,8]. For this reason, many investigations have been performed to understand the occurrence and fate of estrogens in WWTPs[2,3,4,5]. However, these studies were mostly about STPs and there have been very few results on L-WWTPs or H/P-WWTPs globally[2]. Especially, in Korea, a few surveys have been reported on STPs only without the results on L-WWTPs and H/P-WWTPs [6].

In this paper, we investigated estrogens in wastewater to understand their occurrence and fate in various WWTPs (STPs, L-WWTPs, H-WWTPs and P-WWTPs). Target compounds were estrone, 17α-estradiol, 17β-estradiol, estriol and 17α-ethynilestradiol. This is the first study in Korea for understanding of the distribution and behavior of estrogens in wastewater from households, livestock farms, hospitals and pharmaceutical

manufactures.

Materials and Methods

Influent and effluent samples were collected twice from 12 STPs, 4 L-WWTPs, 4 H-WWTPs and 4 P-WWTPs in June and September 2008. The samples were extracted using solid-phase extraction (SPE). Before the extraction, all wastewater samples were filtered with GF/C (Whatman, UK) and adjusted to pH 3 using acetic acid. The samples (500 mL) were spiked with 25 µl of internal standard solution (17β-estradiol-$^{13}C_2$, 10 ng/µl). The SPE cartridges (Strata C18E, 500 mg; Phenomenex, USA) were preconditioned with methanol and water. Then, the samples were loaded onto the cartridges (loading flow: 5 ml/min). The dried cartridges were eluted with methanol, and the extracts were concentrated to 500 µl. The final extracts were analyzed by an 1100 HPLC (Agilent, USA) coupled to an API 2000 LC/MS/MS (Applied Biosystems, USA) with a ZORBAX Eclipse XDB-C18 column (4.6 × 150 mm, 3.5 µm). The analysis was performed in electrospray ionization (ESI), and target analytes were identified and quantified using the multiple-reaction monitoring (MRM) mode. The correlation coefficients (r^2) of calibration curves were over 0.99, and the recoveries of analytes ranged from 70 to 80%. Limits of quantification (LOQ) (signal-to-noise ratio = 10) of target compounds ranged from 0.44 to 9.54 ng/L.

Results and Discussion

Distribution of estrogens in wastewater

Table 1 shows the concentrations of estrogens in the influents and the effluents collected from target STPs, L-WWTPs, H-WWTPs and P-WWTPs. In the influents, the L-WWTPs (0.195−10.424 µg/L) and the STPs (0.028−1.151 µg/L) showed higher total concentrations of estrogens than the other WWTPs (H-WWTPs: 0.068−0.130 µg/L, P-WWTPs: 0.015−0.070 µg/L). Especially, the waste water from livestock farms, known that large amounts of animal waste are generated, has the highest levels of estrogens.

STPs

In the STP influents, estrone (0.013−0.052 µg/L) and estriol (0.046−1.130 µg/L) were detected in over 20 of 30 samples, while the other estrogens didn't detected except for only one case (17β-estradiol: 0.017 µg/L). The similar results have been reported by many foreign studies. In Italy, the concentrations of estrone (0.025−0.132 µg/L) and estriol (0.024−0.188 µg/L) in STP influents were higher than those of 17β-estradiol (0.004−0.022 µg/L) and 17α-ethynilestradiol (<0.001−0.013 µg/L), and the levels of estriol were lower than those in this study[4]. The concentrations of estrone (0.019−0.078 µg/L) and 17β-estradiol (0.002−0.026 µg/L) in the STP influents of Canada were similar to the result in this study[3]. In the effluents, estrone (0.001−0.079 µg/L) was detected in 16 of 34 samples, estriol (0.160−0.273 µg/L) in three effluent samples, and the others were not detected. The levels of estrogens in the STP effluents were below 1 µg/L in other countries like this study[3,4].

L-WWTPs

Estrone (0.169−8.150 µg/L) and 17α-estradiol (0.026−0.766 µg/L) were found in all 8 influents, followed by 17β-estradiol (0.064−0.634 µg/L) and estriol (0.146−2.280 µg/L) in 6 samples. In the L-WWTP effluents, estrone (0.003−0.529 µg/L) was detected in 4 of 8 samples and estriol (0.200 µg/L) was in 1. It is unavailable to compare the levels of estrogens in the L-WWTP with those of other studies due to lack of previous researches.

H-WWTPs

The H-WWTPs had lower levels and frequencies of detection of estrogens than those in the STPs and the L-WWTPs. Estriol (0.068−0.124 μg/L), estrone (0.006 μg/L) and others (ND) were detected in 2 or less samples of 12 influent samples. In the H-WWTP effluents, estrone (0.002−0.006 μg/L) was found in 2 of 8 samples, estriol (0.015 μg/L) in 1, and others were not detected. In Norway, estrogens in the hospital effluents were surveyed, and their levels were below 1 μg/L like the result in this study[7].

P-WWTPs

Like the H-WWTPs, the P-WWTPs also showed lower levels and frequencies of detection of estrogens than those in the STPs and the L-WWTPs. Estrone (0.011−0.015 μg/L) and estriol (0.059 μg/L) were detected in 2 and 1 of 8 influent samples respectively. In the P-WWTP effluents, only estrone (0.011 μg/L) was found in 1 of 8 samples. Like L-WWTPs, it is hard to compare the result in P-WWTPs with those in other researches.

Removal of estrogens in STPs and WWTPs

The removal efficiencies of estrogens in target STPs and WWTPs were summarized in Table 2. It is known that estrogens generally have significant removal efficiencies in WWTPs because of biological degradation[3,4]. In all STPs and WWTPs surveyed in this study, biological treatment processes were operated as major wastewater treatment processes. In most of cases, estriol showed fine removal efficiencies at over 80% regardless of WWTP types. Estrone had wider range of the removal efficiencies than estriol. In the STPs, the removal rates of estriol were over 90% in 25 of 28 cases, while estrone showed the removal efficiencies at over 90% in 13 of 26 cases. Thus, in this study, estrone seems to have lower removal efficiencies compared with other studies. 17α-Estradiol and 17β-estradiol were detected in most of L-WWTPs, and their removal rates were over 90% except for 1 case. In the case of 17α-ethynilestradiol, the removal efficiencies could not be calculated because it was not detected in all samples.

Acknowledgments

This work was supported by the National Institute of Environmental Research (NIER) and the Korea Science and Engineering Foundation (KOSEF) grant funded by the Korea government (MEST) (No. R01-2007-000-10507-0).

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Table 1. Concentrations of estrogens in wastewater samples (unit: μg/L)

	Estrone	17α-Estradiol	17β-Estradiol	Estriol	17α-Ethynilestradiol
STPs					
Inf.	0.029[a] (23/30)[b] (0.013−0.052)[c]	ND	0.017 (1/30)	0.379 (25/30) (0.046−1.130)	ND
Eff.	0.019 (16/34) (0.001−0.079)	ND	ND	0.206 (3/34) (0.160−0.273)	ND
L-WWTPs					
Inf.	3.648 (8/8) (0.169−8.150)	0.299 (8/8) (0.026−0.766)	0.237 (6/8) (0.064−0.634)	0.656 (6/8) (0.146−2.280)	ND
Eff.	0.164 (4/8) (0.003−0.529)	ND	ND	0.200 (1/8)	ND
H-WWTPs					
Inf.	0.006 (1/12)	ND	ND	0.096 (2/12) (0.068−0.124)	ND
Eff.	0.004 (2/8) (0.002−0.006)	ND	ND	0.015 (1/8)	ND
P-WWTPs					
Inf.	0.013 (2/8) (0.011−0.015)	ND	ND	0.059 (1/8)	ND
Eff.	0.011 (1/8)	ND	ND	ND	ND

ND: not detected
[a] mean concentration, [b] frequency of detection, [c] range of concentrations

Table 2. Removal efficiencies of estrogen in STPs and WWTPs

	E1	α-E2	β-E2	E3	EE2		E1	α-E2	β-E2	E3	EE2
STPs						***H-WWTPs***					
Target	26	0	1	28	0	Target	2	0	0	1	0
~ 90%	13	0	1	25	0	~ 90%	0	0	0	0	0
80 ~ 90%	1	0	0	0	0	80 ~ 90%	0	0	0	1	0
60 ~ 80%	3	0	0	0	0	60 ~ 80%	0	0	0	0	0
40 ~ 60%	1	0	0	0	0	40 ~ 60%	0	0	0	0	0
0 ~ 40%	4	0	0	0	0	0 ~ 40%	0	0	0	0	0
NR	4	0	0	3	0	NR	2	0	0	0	0
L-WWTPs						***P-WWTPs***					
Target	8	8	6	6	0	Target	3	0	0	1	0
~ 90%	6	8	6	5	0	~ 90%	2	0	0	1	0
80 ~ 90%	0	0	0	0	0	80 ~ 90%	0	0	0	0	0
60 ~ 80%	1	0	0	0	0	60 ~ 80%	0	0	0	0	0
40 ~ 60%	1	0	0	0	0	40 ~ 60%	0	0	0	0	0
0 ~ 40%	0	0	0	0	0	0 ~ 40%	0	0	0	0	0
NR	0	0	0	1	0	NR	1	0	0	0	0

E1: estrone, α-E2: 17α-estradiol, β-E2: 17β-estradiol, E3: estriol, EE2: 17α-ethynilestradiol
NR: not removed