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Evaluation of estrogenic hormones in water reservoirs and municipality treatment plants in Istanbul

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ABSTRACT

The increase in population and industrialization has led to increase wastewater treatment plants (WWTPs). Turkey's pharmaceutical sector has grown by over 30% in the last decade, therefore the levels of estrogenic hormones are also expected to increase in wastewater. When exposed from external sources, estrogenic hormones may cause endocrine disturbance. This paper assesses the levels of 17β-estradiol and estrone levels in treatment plants. A total 16 treatment plants and 4 water reservoirs were analysed for 17β-estradiol and estrone using the Enzyme-Linked Immunosorbent Assays (ELISA) test method. 17β-estradiol and estrone values were detected in the range of 37–382 ng/L and <1–187 ng/L, respectively. Pre-treatment plants had the highest levels estrogenic hormones, while reservoirs had the least levels.

Keywords: Endocrine disrupters; 17β-estradiol; Estrone; Estrogenic hormone; Wastewater

1. Introduction

Endocrine-disrupting substances alter the function of the endocrine system which causes diverse health effects to organisms or its progeny when received from outside compounds [1]. Scientists have reported that, endocrine disrupting substances replicate hormones, inhibit or increase the hormone facilities and may have fetal effects on human and animal reproductive systems [2,3]. It is well known that pharmaceuticals and personal care products (PPCPs) have endocrine disrupting effects [4]. Moreover, some natural originated estrogen sources (estrone (E1), 17β-estradiol (E2), estriol (E3), phytoestrogens) and many synthetic estrogen compounds (alkylphenol, pesticide, polichlorinebiphenol, phthalates, bisphenol-A, 17α-ethinylestradiol (EE2), etc.) have been reported to have estrogen-like effects. The most naturally occurring estrogens are 17β-estradiol and estrone [5].

Some endocrine disrupter chemicals which can be found and accumulate in the environment are classified as:

- Natural estrogen (17β-estradiol, estrone, phytoestrogens, steroids, etc.)
- Synthetic estrogens
- Hormones and metabolites (estradiol, testosterone, progesterone)
- Organochlorined pesticides (dikloro difenil trikloroethan (DDT), lindane, atrazine)
- Pharmaceuticals and personal care products (PPCP's)
- Halogened aromatic hydrocarbons (HAH)
- Polycylic aromatic hydrocarbons (PAH)
- Phthalates
- Phenols
- Dioxines, polychlorined biphenols (PCB)
- Alkylphenols
- Alkylphenol etocsilates (APE)
- Fecal steroids
- Antidepressants
- Some heavy metals like cadmium and lead [6–9].

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Table 1 shows the chemical and physical properties of 17β-estradiol and Estrone [10].

In aquatic ecosystem, endocrine-disrupting hormones found in surface water causes feminization of male fish, thus limiting the reproduction. In addition, these hormones causes a decrease in ovulation number in female fish and genetic anomalies in aquatic microorganisms [11]. Endocrine disrupting hormones are on rise in food chain due to the fact that effluent sludge from treatment plants contains considerable amount of such hormones and this compost sludge is mixed with soil [12]. In mammals, exposure to estrogen during fetal or neonatal period cause testicular cancer, puberty, female reproductive system disorders, and low sperm quality [13,14].

Fig. 1 shows the progress of synthetic hormones from excretion system of human to treatment plant influent. Both treatment sludge and effluent of plant plays a great role in the distribution of these hormones to the environment [15].

Hormones are transported to the natural environment directly (effluent water of treatment plants) or indirectly (agricultural originated surface waters). The main source of the hormones in the aquatic environment are via human and animal excretion system [16,17]. Estrogenic hormones; estrone (E1), 17β-estradiol (E2) and estriol (E3) are also found in humans in cholesterol. E1 is the dominant hormone in women in menopause. E2 is the most active female hormone in pre-menopausal periods and has the highest estrogenic potential. E3 metabolism originates from E1 and E2 hormones [18].

Some micro pollutants are absorbed in sludge during wastewater treatment. Degradation of these micro pollutants depends on the treatment technology and are usually found in supernatant, therefore disposed of as recycled in the plant or stabilized with waste sludge [19]. Sewage sludge may contain many anthropogenic organic chemicals. Also land spreading, charging empty mines or agricultural usage of sewage sludge in Turkey, brings the risk of contamination of these organic chemicals to groundwater by rainwater [20]. These organic chemicals may accumulate in the food chain cause of disposal method of sludge [21]. Research on this subject has shown that pharmaceuticals has a resistance to anaerobic degradation [22,23]. Another study shows that significant levels of estrogen can still be found in influent and effluent of the system and disintegrate under methanogenic conditions [24]. Researchers observed that 17β-estradiol concentrations and estrogen activities were greater in effluent wastewater from plant in sludge dewatering process [25]. Researchers have reported that, the synthetic hormone, 17α-estradiol, is measured as 11 ng/g in classic activated sludge system treatment plant sludge. This study also identified the three estrogenic hormones (E1, E2 and EE2) in activated sludge and sewage sludge, even though they haven't reported in effluent [26]. 17β-estradiol and estrone which are estrogenic hormones,

Table 1
Chemical and physical properties of 17β-estradiol and estrone

	17β-estradiol	Estrone
CAS (Chemical Abstracts Service) number	50 – 28 – 2	53 – 16 – 7
IUPAC name	17β-estra-1, 3, 5(10) – trien-3,17-diol	3-hydroxiestra-1, 3, 5(10) – trien-17-1
Molecular weight (g/mol)	272.4	270.4
Chemical formula	$C_{18}H_{24}O_2$	$C_{18}H_{22}O_2$
Physical condition in room temperature	Solid	Solid
Solubility in water (20°C)	13 mg/L	30 mg/L

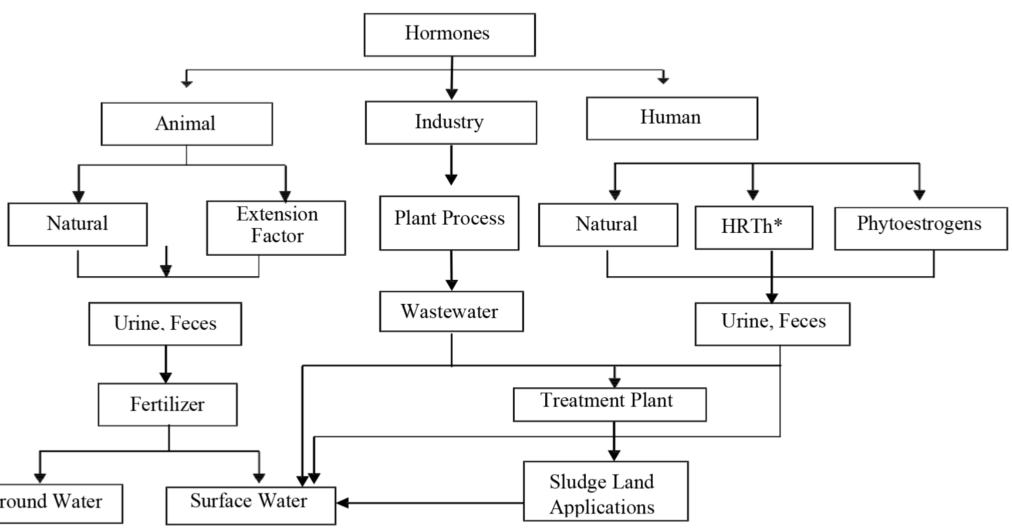

Fig. 1. Distribution of hormones to the environment [15].

were rapidly absorbed into activated sludge from aqueous phase [5].

Research has shown that there is considerable amount of estrone (E1), 17β-estradiol (E2) and 17α-ethinestriol (EE2) in inlet and effluent of WWTPs worldwide. Especially, 17β-estradiol and estrone amounts are substantially high in WWTPs. A study in Canada found that the endocrine disrupting hormone identification in conventional activated sludge treatment plant for 17β-estradiol and estrone values were as high as 26 and 78 ng/L in the influent, whereas in the effluent they were at maximum of 15 and 96 ng/L, respectively [25]. In this study, removal of 17β-estradiol was found to be greater than 75%. Although estrone removal was not clear, and higher in some effluent than in the influent, 98% removal efficiency was achieved in some treatments. This can be explained by the fact that adsorption of hormones in sludge occurs easily [25].

A study of 17β-estradiol concentrations in 12 activated sludge treatment plants in Australia reviewed that, the levels of 17β-estradiol were as high as 44.5 ng/L. The Enzyme-Linked Immunosorbent Assays (ELISA) test method was used for measuring the concentrations. The highest concentrations of 17β-estradiol were reported in treatment plants situated in densely populated region [26]. Research in China showed 6 kinds of different estrogenic hormones were released from industrial WWTP. The most noticeable of these hormones were E1, E2 and EE2, and the WWTP effluent concentrations were 29–129 ng/L, 1126–1170 ng/L and 2193–4437 ng/L respectively [27]. In Jiulongiiang River (China), E1 and E2 concentrations were found to be 321.02 and 74.4 ng/L, respectively [28]. The effluent amount of 17β-estradiol and estrone in the WWTPs in European Union member states, were found to be in the highest values range of 6.5–13 and 35–50.5 ng/L respectively [29]. In a major municipal sewage plant in Germany the 17β-estradiol equivalent concentrations were measured 58 and 70 ng/L in the influent [30].

With a population of over 15 million, there is little information about the levels of estrogenic hormones in Istanbul, Turkey. Therefore, this study aims at establishing the concentration of estrogenic hormones in wastewater and drinking water treatment plants and water reservoirs in Istanbul.

2. Materials and methods

Samples from16 different treatment plants and 4 different water reservoirs in Istanbul-Turkey were collected as shown in Fig. 2.

Samples were bottled in opaque brown glass sampling bottles and were stored at +4°C according to storage conditions determined in Standard Methods. Of these facilities; Büyükçekmece Lake, Terkos Lake, Ömerli and Alibey dams are water reservoirs, while Baltalimanı, Büyükçekmece, Yenikapı, Küçükçekmece, Kadıköy, Üsküdar and Küçüksu are wastewater pre-treatment. Bahçeşehir and Tuzla are conventional classical activated sludge treatment, while Ataköy, Paşaköy and Terkos are advanced biological wastewater treatment. Kağıthane, İkitelli, Büyükçekmece and Ömerli operate as drinking water treatment plants. All samples were collected in spring and on sunny days.

Samples of 17β-estradiol and estrone hormones were analyzed using the ELISA microplate reader at a wavelength of 450 nm. DRG- diagnostics kits were used to measure the concentration of 17β-estradiol, while Dia-Metra brand ELISA kits were used to measure estrone concentrations. Values were calculated by DNM-9602 Perlong ELISA microplate reader and controlled by double check system.

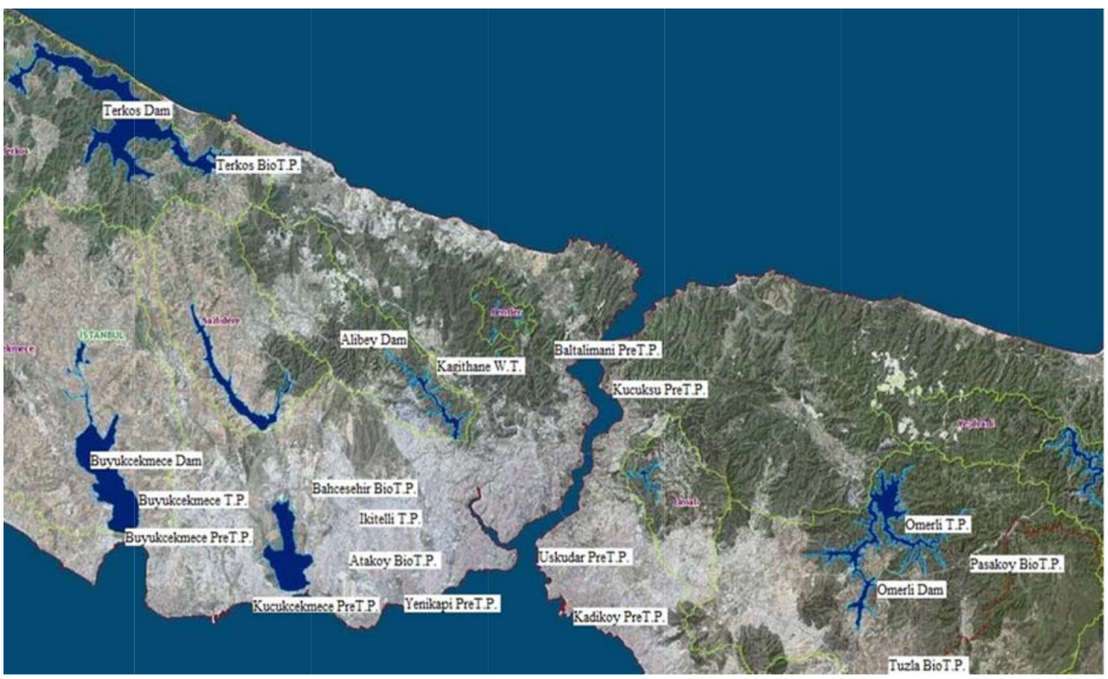

Fig. 2. Locations of treatment plants and water reservoirs in Istanbul, Turkey.

3. Results and discussion

Scope of the study; samples were taken from influent and effluent of drinking water treatment plants, water reservoirs, water dams and wastewater treatment plants in Istanbul. The levels of 17β-estradiol and estrone hormones were determined and results are shown in Table 2.

As shown in Table 2, drinking water treatment plants had the least influent and effluent concentration of 17β-estradiol ranging from 44 ng/L to 55 ng/L for influent and 37 ng/L and 50 ng/L for effluent. Pre-treatment plants have the least removal efficiency of 17β-estradiol (8–22%). This low removal capacity can be attributed to poor technology currently available at these sites. The concentrations range from 140–382 ng/L in the influents, whereas in the effluent it ranges between 126 and 336 ng/L. Biological wastewater showed the highest removal efficiency of 17β-estradiol (21–54%). Influent and effluent concentration of biological wastewater treatment plant were between 81and 267 ng/L and 49–185 ng/L, respectively. 17β-estradiol concentrations in reservoirs was as low as 42 ng/L.

Estrone influent levels range between 48 and 187 ng/L and 31–180 ng/L for effluent at pre-treatment plants. And for biological treatment plants, concentration levels of influent and effluent range from 80–177 ng/L and 58–125 ng/L, respectively. Both reservoirs and drinking water treatment plants showed almost no estrone concentration. Yenikapı, Üsküdar, and Ataköy have the highest levels of 17β-estradiol and estrone. This attributed to the fact, Yenikapı and Üsküdar regions are among the most populated centers in Istanbul.

Total amounts of endocrine disrupting hormones in water reservoirs shown in Table 3.

Büyükçekmece water reservoir, situated in the heart of Istanbul had the highest levels of 17β-estradiol contamination (Table 3). High concentrations of 17β-estradiol in the watershed means that it is not well preserved.

Table 2
Concentrations of estrogenic hormones in Istanbul preatment plants and water reservoirs

	Treatment plant	17β-estradiol			Estrone		
		Concentration (ng/L)		Removal (%)	Concentration (ng/L)		Removal (%)
		Influent	Effluent		Influent	Effluent	
Pre-treatment	Baltalimanı	147	135	8	127	131	–
	Büyükçekmece	215	187	13	137	123	10
	Yenikapı	382	336	12	187	180	4
	Küçükçekmece	250	254	–	110	92	16
	Kadıköy	207	222	–	48	31	35
	Üsküdar	280	218	22	92	83	10
	Küçüksu	140	126	10	82	71	13
Biological treatment	Ataköy	267	185	30	177	125	29
	Bahçeşehir	263	166	37	80	58	27
	Terkos	81	55	32	90	58	35
	Paşaköy	107	49	54	115	87	24
	Tuzla	206	163	21	161	114	29
Reservoir	Büyükçekmece Lake	45	–	<1	<1		
	Terkos Lake	53					
	Ömerli Reservoir	48					
	Alibey Reservoir	42					
Drinking water Treatment	Kağıthane	45	43	4	<1	<1	
	İkitelli	55	49	11			
	Büyükçekmece	47	50	–			
	Ömerli	44	37	16			

Table 3
Amounts of endocrine disrupters in water reservoirs of Istanbul

Water reservoir	Dam capacity (m^3)	Occupancy rate (%)[31]	Total 17β-estradiol (mg)	Total estrone (mg)
Büyükçekmece	148,943,000	27	18,09.65	40.215
Terkos	162,241,000	42	3,611.48	68.141
Ömerli	235,371,000	35	3,954.23	82.379
Alibey	34,143,000	12	172.08	4.097

Table 4
Discharged endocrine disrupters amounts of treatment plants

	Treatment plant	Treatment capacity (m^3/d)	Discharged hormone	
			17β-estradiol (mg/d)	Estrone (mg/d)
Biological treatment plant	Ataköy	400,000	74	50
	Bahçeşehir	7,000	1.16	0.41
	Terkos	1,500	0.83	0.09
	Paşaköy	500,000	24.5	43.5
	Tuzla	500,000	81.5	57
Pre-treatment plant	Baltalimanı	130,000	17.55	17.03
	Büyükçekmece	155,000	28.99	19.07
	Yenikapı	500,000	168	90
	Küçükçekmece	200,000	50.8	18.4
	Kadıköy	1,400,000	310.8	43.4
	Üsküdar	77,000	16.79	6.4
	Küçüksu	640,000	80.64	45.44

4. Conclusion

As it can be seen from Table 2, maximum removal capacity of 17β-estradiol at treatment plants are calculated as 16%, 54% and 22% in water treatment, biological and pre-treatment plants, respectively. Estrone removal capacity is highest at 35% in biological treatment plants. Therefore, with current technology, estrogenic hormones cannot be removed efficiently from treatment plants in Istanbul. High removal capacity in biological treatment plant is due to the adsorption of disruptive hormones in sludge [19]. In Turkey, sewage sludge are either sanitary landfilled, incinerated or used in agricultural fields [32]. Therefore, sewage sludge should be analysed completely since it contains considerable amounts of estrogenic hormones [33].

Table 2 and Table 4 show that the treatment plants with higher wastewater volume also have higher E1 and E2 concentrations. All of these plants discharge their effluents to Marmara Sea. Annually, a total of 312.28g of 17β-estradiol and 142.62g of estrone discharged into Marmara Sea. Compared to other countries, the levels of estrogenic hormones are higher in Istanbul. Therefore, immediate care is required to preserve the water reservoirs of Istanbul.

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