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Research Article

Effect of seasonal changes on steroid hormones concentrations in the Golden Horn Estuary (Sea of Marmara, Turkey)

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Abstract

In this study, the presence, distribution and concentration of steroidal hormones (Estrone, 17β-estradiol and 17α-ethynylestradiol) were examined in the Golden Horn Estuary (Sea, of Marmara, Turkey) for one year. The bottom and surface water samples were collected seasonally from nine stations in the Golden Horn Estuary. In order to determine the hormone levels, solid phase extraction was applied to the water samples and then these samples were analyzed by HPLC with DAD detector. Recoveries of these hormones ranged from 92–100 % for estuary water.

The highest concentrations of estrone, 17β- estradiol, 17α- ethynylestradiol were measured as 1.069 µg/L, 5.25 µg/L, 1.65 µg/L in Golden Horn, respectively. The concentrations of these three hormones are found higher in bottom water than the surface water and the highest concentrations of all hormones were determined in winter season.

Keywords: Endocrine disrupting compounds, steroid hormones, estuary, seasonal variation

Introduction

Emerging contaminants (ECs) that consist of pharmaceuticals, endocrine-disrupting chemicals (EDCs), industrial chemicals, surfactants, personal care products (PPCPs) are a major concern in many countries (Sarkar et al. 2019). Pharmaceuticals, hormones and PPCPs have been using continuously all around the world. A wide variety of product options and increasing human population have boosted the release of these contaminants into the environment.

Estrogens are known as steroid hormone-chemicals that are responsible for the growth and reproduction system of humans and animals. These hormones are also found in plants and fungi (Hook, 1997). Steroid estrogens can be grouped as synthetic or natural hormones (Fig. 1, Table 1). 17β-estradiol and estrone are natural hormones are secreted by women. 17α- ethynylestradiol is a synthetic compound that is widely used in contraceptive pills and animal feed (Gimiliani et al. 2016).

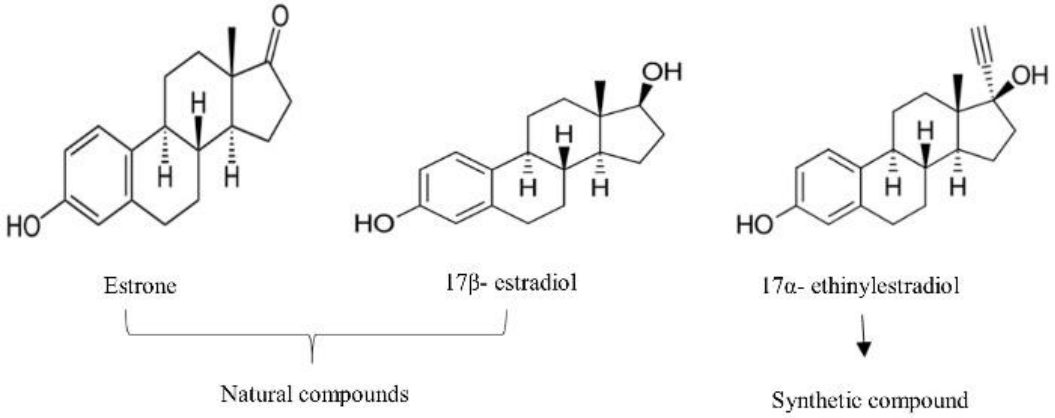

Fig. 1. Chemical structure of steroidal compounds.

Estrogen hormones have a low biodegradability. The solubility of natural estrogens in aquatic environments is approximately 3 mg/L and that of synthetic estrogen is 0.3 mg/L (Roshan and Taghizadeh, 2019). However, some researchers are reported that solubility can be pH-dependent. At pH 10, relative solubilities of estrogens are found higher (Adeel et al. 2017).

Estrogens are commonly found in water supplies such as groundwater, drinking water, surface water and

municipal wastewater also in soil and refined sewage effluents (Mulroy, 2001; Ternes, 2001; Adeel et al. 2017).

Table 1. Physicochemical properties of steroidal compounds (Aydın and Talinli, 2013; Puckowski et al. 2016).

Compounds	Molecular Formula	Molecular (g mol^{-1})	pK_a	Log K_{ow}
Estrone	$C_{18}H_{22}O_2$	270.37	10.5	3.13
17β-estradiol	$C_{18}H_{24}O_2$	272.39	10.6	4.01
17α-ethynylestradiol	$C_{20}H_{22}O_2$	296.40	10.4	3.67

These hormones can enter into the water via domestic wastes, industrial and agricultural activities (Fig.2). This case can lead to public health risks. Especially, the natural estrogens in animal and human waste cause a major threat to the environment. Also, the application of animal manure being an alternative nutrient source for organic farming are increased these risks (Xuan et al. 2008).

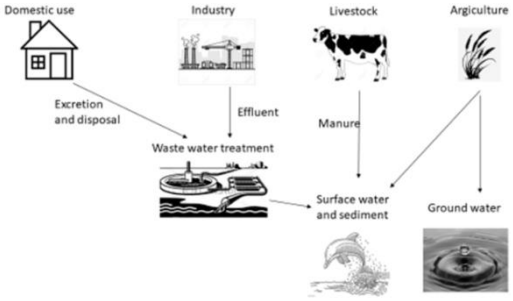

Fig. 2. Sources and pathways of steroidal hormones in the environment

Many studies are performed about the presence of hormones in aquatic environments (Pal et al. 2010, Kolodziej and Sedlak 2007). Although new developments in technology allow detecting even small amounts of these contaminants, the studies that performed so far are not enough to elucidate this environmental problem. The aim of this study to detect the presence, distribution and concentration of steroidal hormones (estrone, 17β-estradiol and 17α-ethynylestradiol) in the Golden Horn Estuary. So far, there have not been any studies showing the presence and concentration of these hormones in the Golden Horn Estuary (Sea of Marmara, Turkey). Therefore, this study provides valuable information for future environmental and human health risk assessment studies.

Materials and Methods

Chemicals, standards and reagents

All of the compounds were of high purity grade (>95% or higher). Steroid hormones; estrone, 17β-estradiol and 17α- ethynylestradiol were purchased from Sigma-Aldrich (Steinheim, Germany). The physicochemical properties of these hormones (molecular formula and weight, pKa and log Kow) are given in Table 1. Stock solutions were prepared in acetonitrile and stored at -20˚C. Methanol and acetonitrile were of HPLC grade and acquire from Merck (Germany). Potassium dihydrogen phosphate was of analytical grade and supplied by Fluka (USA). Solid-phase extraction (SPE) cartridges, packed with 500mg/6mL of Cleanert PEP, were purchased from Agela Technologies (Torrance, USA).

Sample collection

The water samples were collected seasonally from nine stations in the Golden Horn Estuary throughout the year between 2019 and 2020 (Fig. 3 and Table 2). During the sampling, water samples were taken from the two depths, namely, the surface and the bottom, with the Niskin bottles. Primarily, water quality parameters (pH, dissolved oxygen, turbidity, salinity, temperature, secchi depth) were measured during fieldwork. pH, dissolved oxygen, salinity, temperature were measured using the multiparameter device (YSI Professional Plus Multiparameter Instrument). Turbidity was measured using the 2100P turbidimeter HACH device. To analyze the total suspended solids, estuary water was filtered from preweighed GF/F filter papers which were previously dried at 105°C. After filtering, the filter papers were dried again at 105°C and then weighed for calculation total suspended solids concentration (APHA, AWWA, WPCP 1980).

Sample preparation and extraction

Water samples (1 L) was filtered through glass fiber filter papers (GF/F, 0.7µm; Whatman, UK). Before the SPE extraction, liquid-liquid extraction was applied to the samples (100 mL dichloromethane/chloroform (1/1, v/v)). After extraction, the extracts were evaporated to dryness. Ultrapure water (2 mL) was added to the samples. Afterward, solid-phase extraction was performed. The SPE cartridges were conditioned with 4 mL of methanol and 4 mL of deionized water. Water sample (2mL) was loaded to the cartridges. The loaded cartridges were rinsed with 2 mL of deionized water. The elution was performed with 4 mL of methanol and 4 mL of acidic methanol. The obtained eluents were evaporated to dryness then dissolved in 1 mL acetonitrile/water (1/1, v/v). All samples were stored at -20°C until HPLC analysis.

Sampling sites

Golden Horn Estuary was selected as a study area. The Golden Horn is 7 km long and 150–900 m wide (average 370 m) with a surface area of about 2.5×10^6 m^2 (DAMOC 1971; Fig. 3). The water depths decrease from about 40 m at the mouth to 2 m in the innermost estuary. However, some researchers are reported that the main freshwater source to the Golden Horn is only rainfall (Ersan et al. 2011; Gazioğlu et al., 2002; Sur et al. 2002, 2005; Zeki, 2012). Additionally, Bosphorus waters are input via creeks into the estuary from 2012 during remediation works (Istanbul Water and Sewerage Administration, ISKI). Bottom sediment scanning has been carried out continuously in the innermost region as well.

Table 2. The locations of the sampling stations

Stations	Latitudes (°) (N)	Longitudes (°) (E)
GB	41.0220	28.9742
UNK	41.0245	28.9648
KSP	41.0301	28.9562
CA	41.0323	28.9665
VB	41.0404	28.9487
HB	41.0447	28.9435
ES	41.0487	28.9402
BI	41.0530	28.9406
SB	41.0561	28.9444

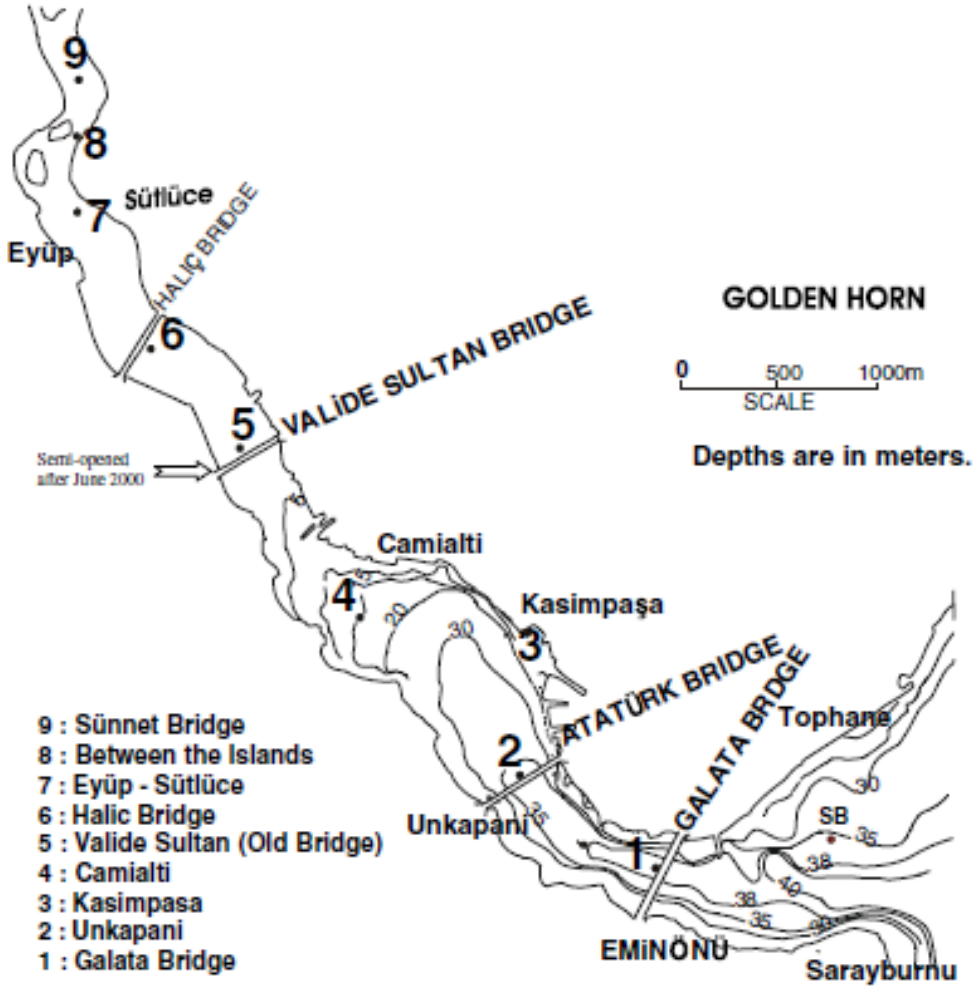

Fig.3. Locations of sample stations in the Golden Horn Estuary (Balkis et al. 2010).

Instrumental analysis

Chromatographic analyses were performed using a HPLC 1100 Series Instrument (Agilent, USA) with diode array detector (DAD) connected online. C-18 (250 × 4.6mm i.d., 5µm thickness) column was used. Results were separated by gradient elution with acetonitrile (A) and a 25 mM potassium dihydrogen phosphate solution (B) at 1.2 mL/min flow rate. The gradient elution program was: 5-18.5% A in 13 mins, 18.5-50% A in 37 mins, 50-55% A in 2 mins held for 5 mins, back to 5% B in 10 mins held for 10 mins. The compounds were measured by the DAD detector and detected as 220 nm. The analysis was completed in 60 min. Method detection limits (MDL) and method quantification limits (MQL) for estrone, 17β-estradiol and 17α- ethynylestradiol, were measured (0.048-0.158 µg/L); (0.031-0.103 µg/L); (0.011-0.036 µg/L) in water, respectively. Recovery (%) of estrone, 17β-estradiol and 17α- ethynylestradiol were 92, 100, 100 respectively in this study.

Results

Surface and bottom water samples were examined in terms of the presence, distribution and concentration levels of hormones. Also, the water quality parameters (pH, salinity, turbidity, total suspended solids (TDS)) were measured seasonally (Table 3a, b).

Table 3a. Seasonal variation of water quality parameters in surface water of the Golden Horn Estuary (Sea of Marmara, Turkey) in 2019-2020.

Seasons	pH	Salinity (‰)	Turbidity (NTU)	TSD (mg/L)
Spring	8.28-8.59	14.48-18	1.94-18.6	8-19.8
Summer	7.85-8.37	11.39-18.65	1.68-9.7	9.3-12.4
Autumn	8.03-8.4	7.4-18.5	1.8-15.6	10-19.5
Winter	7.39-7.79	6.78-19.57	1.9-12.5	7.3-14.1

Table 3b. Seasonal variation of water quality parameters in bottom water of the Golden Horn Estuary (Sea of Marmara, Turkey) in 2019-2020.

Seasons	pH	Salinity (‰)	Turbidity (NTU)	TSD (mg/L)
Spring	8.27-8.75	15.42-32.72	1.8-47.8	7.6-20.2
Summer	7.86-8.36	12.21-32.3	1.83-9	9.6-20.9
Autumn	7.98-8.5	7.51-31.8	1.8-7	9.2-19.5
Winter	7.25-7.74	8.38-32.8	1.96-15.7	8.5-24.6

Terrestrial inputs have been flowed to the Golden Horn due to precipitation in winter. This situation has led to a decrease in pH and salinity.

Surface water

According to obtained data, the concentration of estrone was the range of <0.048 – 1.069 µg/L and the average concentration was found as 0.352±0.1 µg/L in surface water of the Golden Horn Estuary. The highest concentration of estrone was detected as 1.069 µg/L at ES station, in summer season. Moreover, the concentration of estrone in autumn season, was found higher than the other seasons. Secondly, the high values in winter were also measured in both the middle and inner regions. It was found that the concentration levels of estrone were almost similar for all stations (Fig.4).

The concentration of 17β- estradiol was the range of <0.103– 0.71µg/L and the average concentration was found as 0.232±0.09 µg/L in surface water. The highest 17β- estradiol concentration was measured as 0.71 µg/L at HB station in autumn. The concentration of this hormone in spring was found higher than the other seasons. It was determined that the intensity of the 17β-estradiol was higher at the GB, UNK and HB stations which are located in the external and middle region of Golden Horn Estuary, respectively (Fig.4).

For 17α- ethynylestradiol, the concentration was the range of <0.011 – 1.49 µg/L in the Golden Horn Estuary. The average concentration was calculated as 0.376 ± 0.08 µg /L. The highest concentration of this hormone was 1.49 µg/L at the UNK station, in winter. The results also showed that the concentration of 17α-ethynylestradiol in winter season was higher than the other seasons. According to concentration levels, a homogeneous distribution was observed in all stations. (Fig. 4).

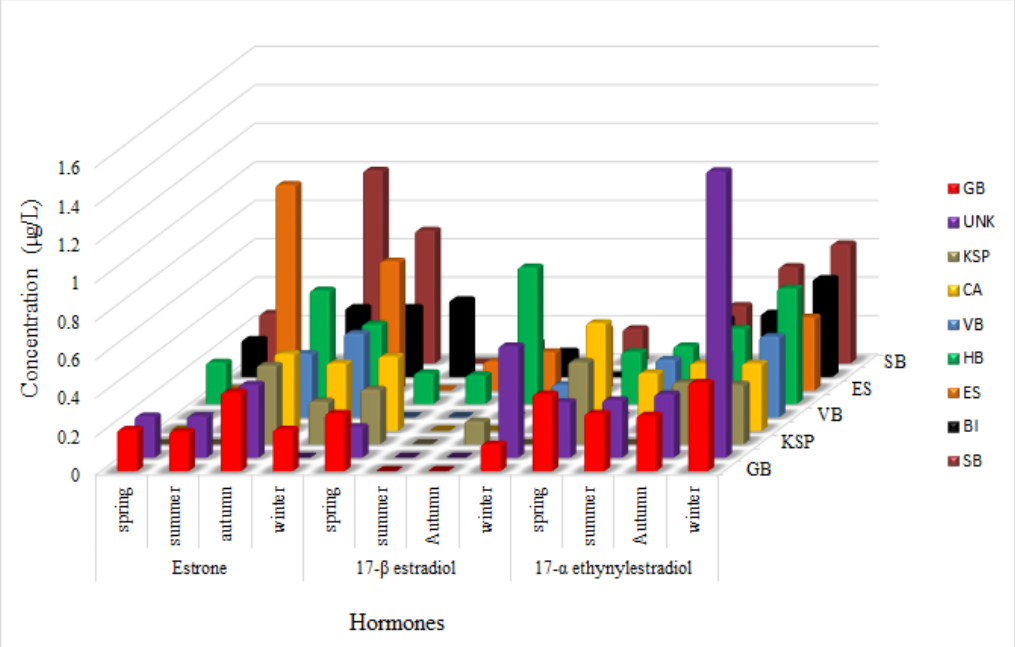

Fig. 4. Total concentrations of steroidal estrogens in surface water samples of Golden Horn during sampling periods. GB, Galata Bridge; UNK, Unkapanı; KSP, Kasımpasa; CA, Camialtı; VB, Valide Sultan Bridge; HB, Halic Bridge; ES, Eyüp-Sütlüce; BI; Between Islands; SB, Sünnet Bridge.

According to the general distribution of natural and synthetic hormones in the surface water, it was found that the concentration of 17α- ethynylestradiol was higher than the other hormones. The highest value was observed in winter and measured as 1.49 µg/L at the UNK station. Besides, the concentration values of these three hormones showed an increasing distribution from the outer part of the Golden Horn Estuary to the inner part (GB-SB) (Fig. 4).

Bottom water

The concentration of estrone was ranged from <0.048 - 0.81 µg/L and the average value was calculated as 0.336 ± 0.11 µg/L in bottom water. The highest concentration was determined as 0.81 µg/L at the SB station in winter season. The concentrations of estrone in bottom water, were higher in autumn and winter seasons than spring and summer seasons. Moreover, the intensity of the estrone was higher at the UNK, HB and SB stations which are located in the external, middle and internal regions of Golden Horn Estuary, respectively (Fig.5).

The concentration of 17β- estradiol in bottom water was found in the range of <0.103–5.25 µg/L. The average value was 0.196±0.05 µg/L. The highest concentration of 17β- estradiol was 5.25 µg/L at the SB station in winter season. It showed that the value of 17β- estradiol in winter was higher than the other seasons (Fig.5).

The concentration of 17α- ethynylestradiol was the range of <0.011 - 1.65 µg /L and average concentration was 0.335 ± 0.09 µg/L. The highest concentration of 17α-ethynylestradiol in bottom water was measured as 1.65 µg/L at the SB station in winter. Also, a homogeneous distribution was observed in concentration levels of 17α-ethynylestradiol during all seasons (Fig.5). It was found that the concentration of 17α- ethynylestradiol was higher at the SB station than the other stations (Fig. 5) and the highest concentration was measured as 1.65 µg/L in winter season (Fig. 5).

The results showed that the presence and concentration of steroidal hormones in bottom water were higher than the surface water. The general distribution of hormones in terms of concentration levels can be shown as 17α-ethynylestradiol> estrone> 17β- estradiol in surface and bottom water of the Golden Horn Estuary (Fig. 4 and 5).

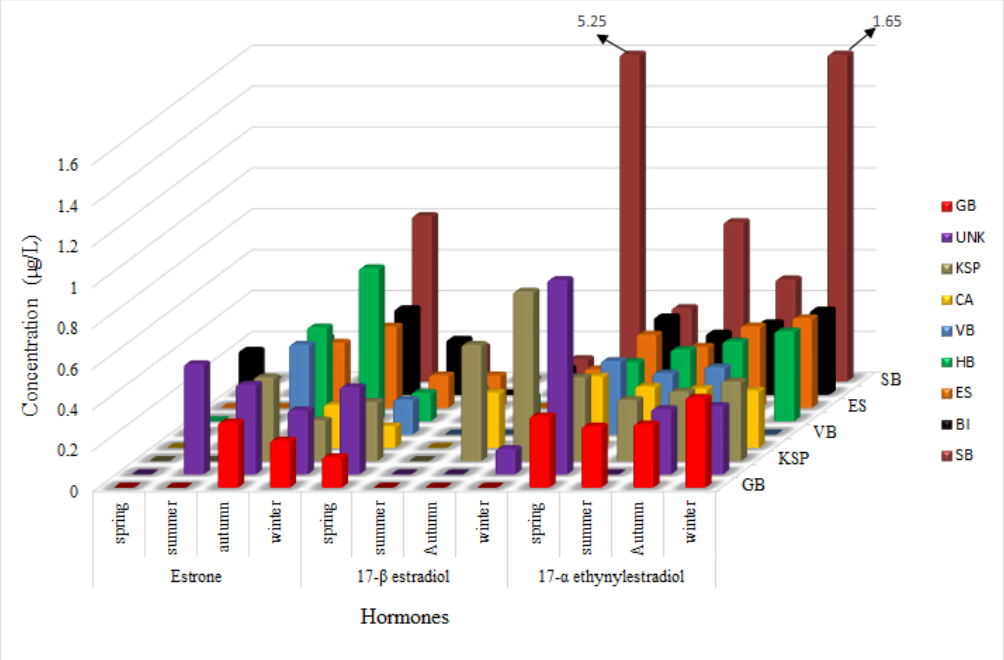

Fig. 5. Total concentrations of steroidal estrogens in bottom water samples of Golden Horn during sampling periods. GB, Galata Bridge; UNK, Unkapanı; KSP, Kasımpasa; CA, Camialtı; VB, Valide Sultan Bridge; HB, Halic Bridge; ES, Eyüp-Sütlüce; BI; Between Islands; SB, Sünnet Bridge.

Discussion and Conclusion

The existence, distribution and concentration of estrone, 17-β estradiol, 17-α ethynylestradiol in the surface and bottom water of the Golden Horn Estuary (Sea of Marmara, Turkey) were examined on a yearly basis. Sampling were performed seasonally (on April 2019, June 2019, October 2019, January 2020). The results showed that the highest concentration in surface water belonged to 17-α ethynylestradiol. This concentration of 17-α ethynylestradiol was measured as 1.49 µg/L at UNK station in winter season (Fig.4). For the bottom water, the highest concentration belonged to 17-β estradiol. This value was measured as 5.25 µg/L at SB station in winter season. Secondly, 17-α ethynylestradiol was determined and measured as 1.65 µg/L at the same station (Fig.5). Previous studies indicated that the high hormone concentration levels in winter came up due to the increase in wastewater input based on rainfalls and the suppression of bacterial activities at low

temperatures (Kim and Carlson, 2007; Yang et al., 2011a,b; Yan et al., 2013). A variety of factors such as the flow rate of input surface water (stream, lake, etc.), switching to sediment or particulate matter, biodegradation, photodegradation and wastewater treatment processes might affect the pharmaceutical concentration in surface waters (Lindholm-Lehto et al., 2016; Moreno-González et al., 2014). Some of these processes such as photodegradation or biodegradation depend on environmental factors (temperature, sunlight and nutrient) (Lindholm-Lehto et al. 2016). Therefore, seasonal variations cause changes in the concentration of pharmaceuticals in surface waters and environmental transport (Paíga et al. 2016).

In winter season, the concentration of estrone was found at high levels in the surface and bottom waters at all stations in Golden Horn Estuary. Also, the concentrations of 17-β estradiol and 17-α ethynylestradiol in bottom waters were high (Fig. 4 and 5). According to Turkish State Meteorological Service data, intensive rain transitions were seen in this region for one week before the sampling time (14.01.2020) (https://www.mgm.gov.tr). These transitions led to uncontrolled anthropogenic terrestrial inputs around the Golden Horn Estuary. High hormone levels suggest that terrestrial inputs carried by rain might carry micropollutants. Furthermore, the significant changes in the water quality parameters [especially pH (7.39-7.79), secchi depth (0.4-4 m) and salinity (6.78-19.57 ‰) decrease in surface water] were observed in winter months (Table 3a). This case supports that the terrestrial input reaches to the receiving environment in winter. The distribution and concentration of these three hormones were examined in surface and bottom water and observed an increasing distribution from the outer to inner part (GB-SB) of Golden Horn (Fig. 4 and 5).

Balkis et al. (2010) reported that the total suspended solids values are higher especially in the inner part of the Golden Horn (ES-SB). Streams, precipitation and terrestrial inputs through the biological activities are responsible for controlling the distribution in the inner regions. In this study, the highest value of total suspended solid (24.6 mg/L) was determined in bottom water at the Sünnet Bridge, in winter season. Similarly, Balkis et al. (2010) reported the highest total suspended solids in the bottom water at Sünnet Bridge station. The high level of total suspended solids indicated that the intense organic, terrestrial and human-induced burdens (micropollutants; hormones) originating from streams and precipitation accumulates in the inner region of the Golden Horn.

Consequently, the determination of the high concentration of total suspended solids in the bottom water of the Sünnet Bridge support to find higher concentrations of estrone, 17β- estradiol, 17α-ethynylestradiol (0.81, 5.25, 1.65 µg/L, respectively) at this station. Also, the high concentration of 17β-estradiol (5.25 µg/L) in bottom water at SB station indicates extremely conditions (such as heavy precipitation, uncontrolled terrestrial inputs) (Fig. 5).
The estrone concentration is usually found higher than 17β- estradiol concentration in wastewater treatment plants (Chang et al., 2011; Jin et al., 2008). 17β-estradiol can easily be oxidized to estrone in the environment (Andersen et al., 2003). This case causes to find a high concentration of estrone hormone in the estuary (Shi et al., 2014).

In this study, the general distribution of natural and synthetic hormones in terms of concentration levels in the Golden Horn in surface and bottom water was determined as 17α- ethynylestradiol> estrone> 17β-estradiol (Fig. 4 and 5). Similar results were reported by Shi et al. (2014) (Table 4).

Table 4. Summary of estrogen concentrations in water in the World.

Regions	Sample type	Estrone	17β- estradiol	17α- ethynylestradiol
South-Eastern Australia	Tidal estuary water	-	-	<0.03- 0.12 ng/L
China	Estuary water	BLD (ng/L)	BLD-75.8 ng/L	BLD- 9.22 ng/L
Northern France	Estuary water	0.37-10 ng/L	BLQ	BLQ
Malaysia	Surface estuary water	<0.56-1.95 ng/L	<5.28- 31.43 ng/L	<0.3- 7.67 ng/L
USA	Estuary water	0.78-1.2 ng/L	0.58-0.83 ng/L	3.01-4.67 ng/L
East China	Estuary water	ND-10.0 ng/L	ND	-
Büyükçekmece Watershed, Turkey	Water	BLD -6.04(ng/L)	BLD-10.2(ng/L)	BLD-14(ng/L)
This study	Estuary water	<0.048- 1.06 µg/L	<0.031-5.25 µg/L	<0.011-0.95 µg/L

BLD: below limit of detection, BLQ: below limit of quantification, ND: not dedected.

Previous studies pointed out that the main source of steroidal hormones in the aquatic environment is the excretion of humans and animals (de Mes et al., 2005; Jobling et al., 2006). In this study, the seasonal distribution of 17α- ethynylestradiol in the surface and bottom water of Golden Horn Estuary was found higher than the other hormones (Fig. 4 and 5). 17α-ethynylestradiol is also known as birth control pills so these pills are mostly used by women. Therefore, pharmaceutical wastes might reach to the Golden Horn

through uncontrolled discharges and precipitation. Also, previous studies support these results (Ying et al. 2003).

The results obtained in this study compared with the hormone values determined in estuarine, gulf and watershed waters around the world and the results are shown in Table 4. The concentrations of hormones detected in the Golden Horn Estuary (Turkey) were found quite high (Table 4). Estrone, 17β- estradiol and 17α- ethynylestradiol concentrations were determined as [BLD], [BLD-75.8], [BLD- 9.22] ng/L in China (Ashfaq et al., 2019); [0.37-10], [BLQ], [BLQ] ng/L in Northern France (Noppe et al., 2007); [<0.56-1.95], [<5.28-31.43], [<0.3- 7.67] ng/L in Malaysia (Hanun Ismail et al., 2019); and [0.78-1.2], [0.58-0.83], [3.01-4.67] ng/L in America (Zuo et al., 2006) respectively. Also, the concentration of 17α-ethynylestradiol was found as [<0.03-0.12] ng/L in South-Eastern Australia (Ferguson et al., 2013). A limited number of studies are carried out in Turkey related to aquatic environments (lakes, seas and bays). Aydın and Taninli (2013) reported lower concentrations of hormones in Buyukcekmece Lake in Turkey compared this study (Table 4). The results obtained in this study point out that even though the bottom screening and improvement studies have been carried out to the Golden Horn, Istanbul regularly since 1994, still uncontrollable inputs have been reached the receiving environment.

The presence, distribution and concentration of natural and synthetic hormones were determined in the Golden Horn on a yearly basis. The following conclusions can be drawn from the obtained data.

- The highest concentrations for all hormones were determined in winter seasons.
- The highest concentrations of estrone, 17β-estradiol, and 17α- ethynylestradiol were measured as 1.069 µg/L, 5.25 µg/L, 1.65 µg/L in the Golden Horn, respectively.
- The highest concentration in hormones belonged to 17-α ethynylestradiol and was measured as 5.25 µg/L at Sünnet Bridge station.
- The concentrations of hormones are found higher in bottom waters than the surface water.
- The general distribution of hormones in terms of concentration levels in Golden Horn Estuary (Sea of Marmara,Turkey) was determined as 17α-ethynylestradiol> estrone> 17β- estradiol.

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