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OCCURRENCE OF SYNTHETIC AND NATURAL ESTROGENIC HORMONES IN THE AQUATIC ENVIRONMENT

WYSTĘPOWANIE SYNTETYCZNYCH I NATURALNYCH ESTROGENÓW W ŚRODOWISKU WODNYM

Abstract

The article is part of a series of publications discussing prevalence of pharmaceuticals in the aquatic environment. The aim of this study is to describe the problem of the presence of hormonal tablets ingredient 17α-ethinylestradiol and its three natural analogues in wastewater and the environment. Basic information on the substances in question and the concentrations in which these compounds can negatively affect aquatic organisms are provided. In the paper, the authors review the literature data on the presence of estrogenic hormones in wastewater, surface water and groundwater. Penetration through aquifers can lead to accumulation of these compounds in the sediments, which is reflected in the literature.

Keywords: 17α-ethinylestradiol, wastewater, surface water, sediments

Streszczenie

Artykuł jest częścią serii publikacji obejmujących zagadnienia występowania farmaceutyków w środowisku wodnym. Celem artykułu jest opis problemu obecności składnika tabletek hormonalnych 17α-etynyloestradiolu i jego trzech naturalnych odpowiedników w ściekach i środowisku. Przedstawiono podstawowe informacje dotyczące rozpatrywanych substancji oraz stężenia, w jakich te związki mogą negatywnie wpływać na organizmy wodne. Dokonano przeglądu literatury dotyczącej występowania estrogenów w ściekach, wodach powierzchniowych i podziemnych. Podczas przenikania przez warstwy wodonośne może dojść do akumulowania się tych związków w osadach dennych, co znajduje potwierdzenie w literaturze.

Słowa kluczowe: 17α-etynyloestradiol, ścieki, wody powierzchniowe, osady denne

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1. Introduction

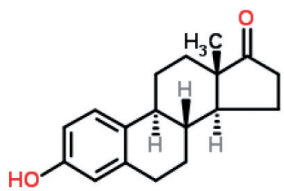
The issue of endangering health and life through contact with water containing even trace amounts of pharmaceuticals is becoming a growing problem for humans and animals. However, the presence of certain groups of pharmaceuticals is more or less controversial than other drugs. And by no means does it depend on the range of concentrations in which these substances are present in the environment, but rather on their impact on aquatic organisms and humans. Despite the high levels at which they occur in the environment, the presence of anti-inflammatory drugs [27] induces less excitement than the presence of hormonal substances. This is primarily due to the fact that the hormonal agents (in particular estrogens) have an extremely adverse effect on living organisms, including fish at a very low concentration of 0.1 ng/l [12]. They affect the feminization of fish [14, 15, 19] inhabiting ponds and rivers, which is a major threat to local ecosystems. These changes are most commonly associated with synthetic hormonal agents, in particular 17α-ethinylestradiol, but also have the effect of natural estrogens such as estrone, estradiol and estriol. All of these compounds are classified as endocrine disrupting compounds (EDC), which interfere with the endocrine system by affecting the synthesis, transport, metabolism and excretion of hormones from the body [17].

2. Characteristic of natural and synthetic estrogens

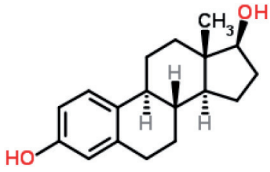
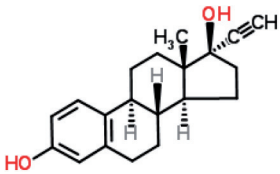
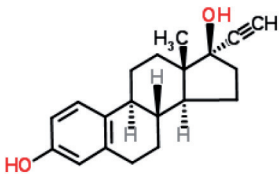
Estrogens are hormone compounds, affecting a range of functions and characteristics of an organism. The natural estrogens include estrone (E1), estradiol (E2) and estriol (E3), while the most common synthetic estrogen is 17α-ethinylestradiol (EE2), a derivative of estradiol. EE2, as a replacement for the natural hormones, is an ingredient in most two-component birth control pills, whose main objective is the inhibition of ovulation. In developed countries, hormonal contraception is one of the most popular methods of protecting against unwanted pregnancy. Table 1 shows the basic information relating to the compounds and Chemical Abstracts Service (CAS) numbers.

Table 1

Characteristics of selected estrogens and their predicted no–effect concentrations (PNEC) [4, 28]

Compound	Formula	Structure	CAS	PNEC [ng/l]
Estrone (E1)	$C_{18}H_{22}O_2$		53–16–7	6

Tab. 1

Estradiol (E2)	$C_{18}H_{24}O_2$		50–28–2	2
Estriol (E3)	$C_{18}H_{24}O_3$		50–27–1	60
17α–Ethinyl-estradiol (EE2)	$C_{20}H_{24}O_2$		57–63–6	0,1

3. Occurrence in the environment

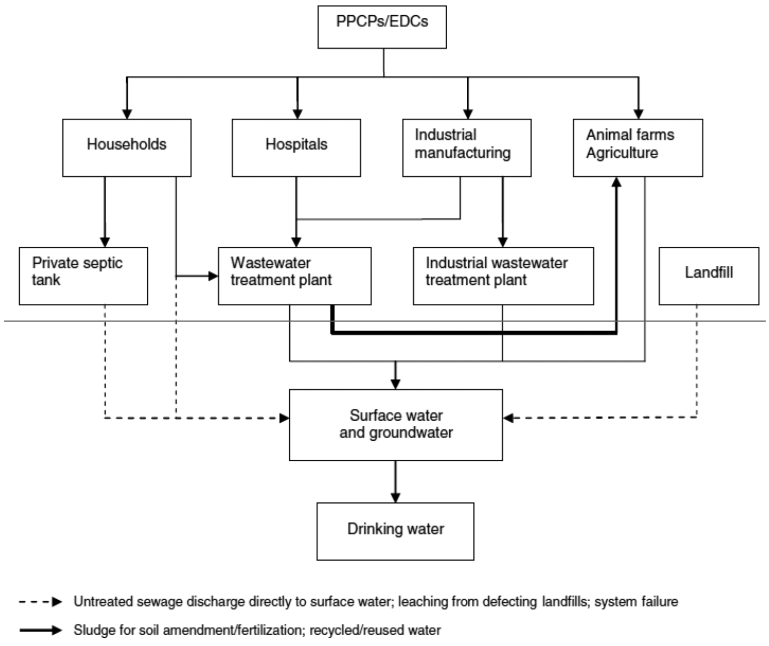


Fig. 1. Sources of endocrine disrupting compounds (EDC), pharmaceuticals and personal care

Potential sources of natural and synthetic hormones are shown in Fig. 1. Every human (especially women) excretes estrogens from the body, even without taking hormonal drugs. For this reason, hormones are expected to be present primarily in wastewater from households, which are transported through the sewer system to the wastewater treatment plant (WWTP). Estrogens, as compounds highly dangerous to the environment, should be degraded and eliminated in wastewater treatment processes with the highest possible efficiency in order to protect aquatic organisms from their harmful influence. Due to the inconstant and complex composition of sewage containing organic substances, wastewater treatment is not an easy task and high effectiveness of their elimination is not always obtained, as confirmed by research carried out in South Africa [23]. Despite up to several tens of percent effectiveness of removal of E1 (72 ± 12%), E2 (78 ± 12%) and EE2 (90 ± 3%) [23], sewage containing from 1 ng/l (EE2) to 107 ng/l (E2) estrogens were released into a river. Comparison of the contents of examined hormones in the river above and below WWTP showed a distinct increase in levels of these compounds (in the case of estradiol – 28 ng/l above and 66 ng/l below the sewage treatment), for which the WWTP is directly responsible [23]. Table 2 shows confirmed estrogen levels in wastewater, surface water and groundwater, with sources of literature.

Table 2

Concentrations in ng/l (min–max or mean) of detected hormones in WWTP influent, WWTP effluent, surface and groundwater

Compound	Influent	Effluent	Surface water	Groundwater
Estrone (E1)	1–670[1] 47–376[8] 2.4–670[11] 10–170[22] 49[25] 5–160[32]	25–42[8] 1–96[11] 36–70[21] 1–80[22] 4.3–12[25] 5–30[32]	1.4–5.74[2] 7–52[3] 22.4–66.2[6] 2.3–77.5[7] 0.45–2.98[13] 0.64–55.3[20] 0.3–5[21] 1.2–10[26] 0.08–78.7[29] 0.5[30] 1–1.45[31] 2.8–321[33] 14–180[35]	1.6–3.5[21] 0.7[30]
Estradiol (E2)	3–3000[1] 31–74[8] 2.4–150[11] 2–50[22] 72–190[24] 20[25]	31–51[8] 0.2–30[11] 9.2–180[21] 1–7[22] 0.4–1.3[25]	1.1–5.39[2] 4.8–48[3] 10–150[5] 1.4–33.9[6] 2.3–10.2[7] 0.28–1.78[13] 21.2[20] 0.31–1.2[21] 1–175[26] 2.3–7.72[29] 0.2[30] 4.41–9.96[31] 3.7–74.4[33] 1–134[35]	0.21–1.6[21] 0.4[30]

Tab. 2

Estriol (E3)	17–1000[1] 74–234[8] 23–660[11] 125–800[22] 90–830[24]	46–175[8] 0.43–275[11] 25–590[21] 270–590[24]	2.15–5.2[2] 10–480[5] 12.4–73.6[6] 2.14–4.37[13] 46.4[20] 0.1–1.9[21] 1.02–1.65[31] 2.3–47.85[33] 4–94[35]	0.16[21]
17α–Ethinylestradiol (EE2)	2–400[1] 0.4–14.4[11] 1–3[22] 70–180[24] 1[25]	0.3–4.1[11] 1.3[21] 1–2[22] 30–180[24] 0.2–0,47[25]	11.7–14[2] 4.3–51[3] 10–280[5] 7.53–27.4[6] 4.3–28.6[7] 0.28–2.67[13] 0.4–24.4[20] 0.33[21] 0.8–34[26] 0.11–53.4[29] 1.4[30] 6.03–10.2[31] 0.52–101.9[33] 7–24[35]	0.94–3[21] 1.2[30]

The presence of estrogens in surface waters is of concern not only because of penetration of these compounds into groundwater, but also as to their accumulation in bottom sediments. Table 3 shows the concentration levels of estrogen in the sediments calculated as a dry mass. These reports confirm an accumulation of natural and synthetic hormones in the sediments in concentrations up to several tens of ng/g dry mass of sediment. It should be noted that, in many cases, the concentration of these highly exceed the PNEC, which means the possible risk of harmful effects on aquatic organisms.

Table 3

Concentrations in ng/g of dry weight (min–max or max) of estrogens in sediments

Compound	Estrone	Estradiol	Estriol	17α-Ethinylestradiol
Level of hormones	0.71–50.75[9] 0.3–1.28[16] 0.4–3.3[18] 0.98–21.6[20] 4.61–11.22[34] 3–10.8[35]	0.87–40.96[9] 0.18–1.58[16] 0.03–1.2[18] 9.7[20] 3.71[34] 1.2[35]	1.26[16] 7.29[20] 1–7.6[35]	133.64[9] 9.26[20] 2–41[26] 2.48[34] 5.1[35]

4. Conclusions

Estrogenic hormones are commonly found in water in quantities greater than the predicted no-effect concentrations showing no impact on living organisms. Despite the use of advanced mechanical and biological methods of wastewater treatment, hormonal substances penetrate into the environment adversely affecting the organisms living in rivers and reservoirs to which treated wastewater is discharged. The progressive feminization of fish and the risk of the harmful effects of eating such fish by humans requires a critical approach to elimination of estrogens in WWTP. Due to the development of consciousness of young people, in particular women, gradual change of approach to contraception and easy access to this form of pregnancy prevention, we should expect a systematic increase in levels of presence of estrogens in wastewater.

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