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# ASSESSMENT OF ENVIRONMENTAL POLLUTION CAUSED BY EDCs FROM EVERYDAY OBJECTS

## OCENA ZANIECZYSZCZENIA ŚRODOWISKA ZWIĄZKAMI EDCs POCHODZĄCYMI Z PRZEDMIOTÓW CODZIENNEGO UŻYTKU

**Abstract:** Endocrine-disrupting compounds (EDCs) are a specific category of chemicals that attracted a great deal of public and scientific attention in the past few decades. They are proved to interfere with the endocrine system, and thus affect the growth, reproduction, homeostasis and metabolism of living organisms. They appear as a threat not only for humans but also for the wildlife. EDCs are present in plastics such as plastic food packaging, detergents, pesticides, fire retardants, heavy metals, pharmaceuticals. They are also components of personal care products, for example cosmetics like creams, soaps or UV filters, oral contraceptives, analgesics and many more. They are not always detected and eliminated in sewage treatment plants and because of that they get to the environment and with the running water into the households. In order to eliminate different contaminants, appropriate techniques have to be chosen.

**Keywords:** EDCs, PPCPs, wastewater treatment

## Introduction

In the past few decades a specific category of chemicals attracted a great deal of public and scientific attention. They appear as a threat not only for humans but also for the wildlife. EDCs (endocrine-disrupting compounds, endocrine-disrupting chemicals) are proved to interfere with the endocrine system, and thus, may affect the growth, reproduction, homeostasis and metabolism of living organisms [1].

In 1997 the US Environmental Protection Agency (US EPA) defined an EDC as "an exogenous agent that interferes with the synthesis, secretion, transport, binding, action, or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction, development, and/or behavior" [2].

The list of EDCs includes: pesticides (*e.g.* DDT - 2,2-bis-*p*-chlorophenyl-1,1,1-trichloroethane, vinclozolin, atrazine), organochlorines and organohalogens (*e.g.* dioxins and furans produced during the incineration of chlorinated aromatic compounds, paper and in production of PVC plastic, brominated fire retardants), alkyl phenols used in production of phenol resins and plastic additives (*e.g.* nonyphenol, nontlphenol etoxylate, octylphenol), bisphenol A, phthalates: higher-molecular-weight phthalates (*e.g.* DEHP - bis(2)ethylhexyl) phthalate, PVC - polyvinyl chloride, DBP - dibutyl phthalate, BBP - butyl benzyl), lower-molecular-weight phthalates (DMP - dimethyl phthalate, DEP - diethyl phthalate), heavy metals (*e.g.* Cd - cadmium, Cu - copper, Pb - lead, Hg - mercury), phytoestrogens (isoflavones, lignans), natural hormones excreted by humans and livestock (*e.g.* (E1) - estrone, (E2) - 17β-estradiol, (E3) - estriol), synthetic hormones (*e.g.* (EE2) - ethinyl estradiol) [3-6].

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**Endocrine disrupting compounds**

Phytoestrogens are natural products classified as endocrine-disrupting compounds - isoflavones, such as: daidzein (Dai) present in soy, genistein (Gen) found in soybeans, lupin, fava beans, kudzu and psoralca, kacmpferol (Kacm) isolated mostly from tea, broccoli, grapefruit and apples. Flavonoides: apigenin (Api) is used to dye wool, coumesterol (Coum), classified as a coumestant, is also able to bind to the estrogen receptors.

Bisphenol A (BPA) is widely used in the manufacturing of polycarbonate and other plastic products, epoxy resin-based food can liners, flame retardants, dental fillings and rubber chemicals. The annual production of bisphenol A is about 3 Tg, of which nearly 100 Mg are released to the atmosphere.

Bisphenol AF (BPAF) is used in production of polycarbonate copolymers in high-temperature composites and electronic materials.

Data shows that bisphenols are detectable in urine samples in more than 90% of the U.S. population.

Higher-molecular-weight phthalates, *e.g.* DEHP, PVC, are widely used in consumer goods, such as food packaging, plastics, detergents and resins.

Widespread exposure for these chemicals (food, air, dust and other goods) may result in adult living beings in reduced fertilization success, miscarriage, premature delivery, reduced sperm quality, gene expression and many other serious disorders [3, 4, 7-10].

Pesticides, including herbicides (*e.g.* alachlor, aminotriazole, atrazine, metribuzin, nitrofen), fungicides (*e.g.* benomyl, carbendazim, hexachlorobenzene, pyrimidine methanol, ethylidene double dithiocarbamate zinc), insecticides (*e.g.* (Endo) endosulfan, (Kep) kepone, lindane(β-666), chlordane, endosulfan, triazine), nematicides (*e.g.* temix, carbofuran, dibromochloropropane (DBCP)) are very extensively used in agriculture. Recently, the usage of herbicides and pesticide in developing countries has been increasing alarmingly. They are present in food and water, and what is the most important, some of them are proven to affect the male reproductive system and to cause cancers. Statistics show that every year there are around 20,000 deaths as a result of acute pesticide intoxications. Because of that, usage of some pesticides have been restricted or banned in industrialized countries. Unfortunately they are often exported to developing countries where such restrictions do not exist [3, 4, 9, 11].

Another group of compound interfering with estrogen receptors are metaloestrogens, commonly used in industrial mining and metallurgy, such as: cadmium, cobalt, copper, nickel, lead, zinc, mercury, tin, chrome and aluminum. Among them cadmium belongs to the most wide spread. It is used in production of batteries, dyes, plastics and is a part of cigarette smoke. Also popular nickel is able to impair the proper thyroid functioning, while zinc, lead and mercury cause reproductive disturbances [10-12].

**Pharmaceutical and personal care products**

Another group of EDCs, which biological effects to nontarget organisms are being currently studied is big group of pharmaceutical and personal care products (PPCPs) used for both humans and animals for daily personal care, disease treatment and prevention. They include: pharmaceutical products, such as: analgesics and anti-inflammatory drugs

(*e.g.* acetaminophen, diclofenac, ibuprofen, ketoprofen and naproxen), antibiotics/antimicrobials (*e.g.* sulfonamides, chlortetracycline, tetracycline, trimetoprim, erythromycin), antiepileptics (*e.g.* carbamazepine), beta-blockers, blood lipid regulators used to lower cholesterol and triglyceride levels in the blood (*e.g.* clofibrate, bezafibrate), cytostatics, contraceptives, antiseptics - chemical agents that slow or stop the growth of microorganisms on external surfaces of the body (*e.g.* triclosan), synthetic musk fragrances commonly used in perfumery(*e.g.* nitromusks, galaxoline, tonalide), sun screen agents (*e.g.* benzophenone, methylbenzylidene camphor, octylmethoxycinnamate), parabens used as preservatives in most cosmetics and other personal care products (*e.g.* methyl-, ethyl-, propyl-, butylparagen), surfactants/alkyl phenols used in emulsifiers production [3, 10, 11, 13].

Parabens are a group of p-hydroxybenzoicacid (PHBA) widely used in cosmetic, pharmaceutical and food industries. The most common is methylparaben due to its antibacterial activity and the fact that it does not modify the physical properties of the final product, such as taste, color or texture. Parabens are found in almost all categories of cosmetics and many pharmaceuticals: soaps, lotions, shampoos, conditioners, creams, tonics, gels, toothpastes, sunscreens, make up cosmetics, ointments, syrups and aerosols. Studies have proved that long-term exposure to these compounds may affect the growth and development of cancerous tissue by absorbing into biological tissues. It can also interfere with secretion of testosterone and functioning of the females' reproductive system [14].

UV filters that provide the protection against the harmful effects of the ultraviolet radiation coming from the sun, are used not only in cosmetics, such as: creams, lotions, lip balms, hair sprays, hair dyes, shampoos, nail polishes but also in tires and inks. Sun screen agents can get into the surface waters directly by recreation activities when cosmetics are rinsed off of the skin by swimming pool or lake water. Even more important is the indirect way - some UV filters stay on clothes and towels and while washing, they get into the domestic sewage. Sun screen agents are commonly detected in samples of surface waters and freshwater fishes [15, 16].

Many of these xenoestrogens enter waste treatment plants via household and industrial waste streams, and due to their insufficient removal processes, they are released to streams and rivers, where they often resist degradation by microbes and ultraviolet light. While the toxicities of other compounds can be reduced by dilution of the effluent in surface waters, EDCs can elicit biological effects at very low concentrations. Except this one, other important factors are persistence, bioaccumulation, exposition time and mechanism of biotransformation. Some compounds in the environment after biotransformation give metabolites or by-products more harmful than the original substances. Researches show that measurable levels of hundreds of substances from pharmaceutical and personal care products are found in the $\mu g/dm^3$ range in sewage-treatment plant effluents and in the $ng/dm^3$ range in surface waters. A lot of endocrine disruptors are hydrophobic, have low vapor pressures, high octanol-water partitioning coefficients, partition into sediment and sewage sludge and have been detected in biosolids. Over 3 million metric tons of these biosolids are applied to agricultural fields, parks and other areas each year.

Xenoestrogens such as bisphenol-A may leach into drinking water from infant bottles and coatings in food cans. Alkylphenols, phthalates and polyaromatic hydrocarbons can get into drinking water when plastic pipes are used in supply lines [1, 3, 6, 11, 13].

**Effect of endocrine-disrupting compounds on humans and environment**

Endocrine disrupting compounds are widely distributed in the biosphere by precipitation, surface runoff, the usage of pesticides and through enrichment of food and drinking water. Even if the content is low, after long time of continuous exposure, the organism response can be similar to that produced by exposure to a higher dose of a single endocrine disruptor. Such compounds cause abnormal and even toxic effects. Exposure to xenoestrogens during critical periods, such as the cellular differentiation period may result in permanent character changes in the mature living beings. Children's developing systems are delicate and they may not be able to repair the damage triggered by EDCs exposure. Reports show frequent occurrence of childhood cancers and congenital malformations among children, whose parents had contact with pesticides at work. Endocrine disruptors in adults may be associated with reduced fertilization success, sperm and embryo quality, implantation failure, miscarriage, premature delivery, endometriosis, altered hormone concentrations, obesity. But xenoestrogens affect not only reproductive function, but also a range of tissues which are steroid sensitive, for instance, the central nervous system and thyroid. They can also interfere with immune system, glucose homeostasis, alter epigenetic markers and gene expression, causing breast, testicle and prostate cancers [3, 6, 9, 11].

It is evident now that exposure to endocrine disrupting compounds is almost unavoidable. Having the potential to bio-accumulate in body fat, they may be released later and enter infants during pregnancy or through breast milk. The effects associate with the presence of xenoestrogens in the environment are: reduced sperm count in males, reduction in the breakage of eggs of birds, fishes and turtles, feminization of male fishes, sexual abnormalities in alligators (due to exposure to organochlorines), reproductive problems in fishes, reptiles, birds and mammals, prostate enlargement in male mice, obesity in offspring and changes in immunologic system of marine mammals. In some cases, these disorders can lead to decline in population [1, 3, 11, 16].

Anadromous salmon population decline is an effect of exposure to anthropogenic disturbances, such as endocrine disruptors, as the salmons pass through some most polluted areas of larger rivers and estuaries during their downstream migration to the sea. The biggest threat seems to be nonylphenol (NP) which is widely used in manufacture of paper, plastic, agricultural chemicals, pesticides, commercial and household cleaning products, detergents, cosmetics, contraceptives and paints, and is commonly released to the environment. Along with other pollution and environmental disturbances, nonylphenol can elicit stress response affecting both metabolic and ion regulatory processes. What is more, polychaetes as feeders in aquatic ecosystems are likely to accumulate xenoestrogens, such 17β-estradiol, nonylphenol, bisphenol A and octylphenol, from sediment through dietary uptake. It is important, because benthic invertebrates are main food source for some bottom feeding fishes.

Another big problem is increasing resistance in the natural bacterial population due to misuse and overuse of antibiotics, their over the counter availability together with crowding and improper sewage disposal [17, 18].

**Endocrine-disrupting compounds removal from wastewater**

Data from recent researches shows that conventional treatment processes removal of endocrine disruptors are sufficient only in around 25% and dependent upon its intrinsic chemical properties such as molecular weight, relative hydrophobicity, aromatic carbon content and functional group composition. The hydrophobic and nonpolar nature of EDCs allows them to absorb onto particulates. This suggests that the general effect of wastewater treatment processes would be concentration of organic pollutants and their removal from the aqueous phase to primary and secondary sludge, by mechanical separation techniques. Wide range of PPCPs, pesticides and alkyl phthalates can be removed using nanofiltration or reverse osmosis. Nanofiltration membranes remove E1 by size exclusion and others by adsorption, however, the membrane retention decreases with increase in the amount of E1 accumulated on the membrane surface.

Effective is application of coagulation by cationic polyacrylamide in water supply, which enhance the removal of phthalate esters and reduce water turbidity. Flocculation is sufficient in dioctyl phthalate removal, and under optimized conditions its effectiveness reaches 82%.

More advanced water treatment technologies, such as granular activated carbon (GAC) adsorption or ozonation are recommended as better way to remove many xenoestrogens including methoxychlor, endosulfan, DDT, dioxin, polychlorinated biphenyls and many others. Even though adsorption, using granular activated carbon is sufficient in removing most organic contaminants (from 60 to 99% for estrogens 17β-estradiol and 17α-ethynylestradiol), some of them, for instance: iopromide, analgesics like ibuprofen, naproxen, dichlofenac, sulfamehtoxazole and meprobamate are recalcitrant for this method. Ozonated activated carbon would oxidize endocrine chemicals into small organic molecules, and thus increase the efficiency of GAC adsorption.

Advanced oxidation processes (AOPs) is a group of chemical-oxidative processes which are characterized by the generation of hydroxyl radicals. Hydroxyl radical, as one of the strongest radicals, is able to oxidize and mineralize almost every organic pollutant into $CO_2$, $H_2O$ and mineral acids. Light oxidation techniques are those which are characterized for the use of UV radiation and the presence of oxidants as hydrogen peroxide and ozone. $UV/H_2O_2$ and titanium dioxide photocatalysis are efficient in removing up to 98% of estrogens, bisphenols and antiepileptics. Ozonation as a dark oxidation treatment eliminates 90% of estrogens, antibiotics, pesticides, anti-inflammatories and antiepileptics from wastewaters. Ozone is considered to be more efficient for PPCPs control than $ClO_2$ or $Cl_2$ which are used in the most widespread conventional treatments.

Activated sludge biological treatment, commonly used in large cities, as numerous studies showed that the majority of endocrine disruptors are biodegradable, is considered as the cheapest available process of removing and degrading compounds. Conventional biological processes, such as activated sludge, biofiltration and soil aquifer treatment exhibit some degree of EDCs removal. They are more efficient in disposing of alkylphenols, bisphenol A and natural estrogens from the aqueous phase than primary treatment. Data indicates that this process can remove around 85-88% of βE2, 85% EE2, up to 95% of E3, however, the removal performance for E1 appears to be less and more variable. Further studies show that the highest removal rates of estrogenic activity were

obtained at plants with comprehensive treatment technologies, for instance combined biological and chemical ones [3, 5, 9, 11, 19].

## Conclusions

This paper presented that most of the everyday objects, such as cosmetics, pharmaceuticals, plastic food packaging, pesticides and many more are sources of compounds interfering with natural endocrine system, causing diverse disorders. Due to the inefficient wastewater treatments, they are widely released to the environment, and even in "acceptable" concentrations, resulting in abnormal changes in wildlife. In order to eliminate different contaminants, appropriate techniques have to be chosen. That is why control and proper removal of endocrine disrupting compounds from sludge should be further studied.

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## OCENA ZANIECZYSZCZENIA ŚRODOWISKA ZWIĄZKAMI EDCs POCHODZĄCYMI Z PRZEDMIOTÓW CODZIENNEGO UŻYTKU

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**Abstrakt:** Związki modulujące pracę hormonów estrogenowych są grupą związków chemicznych, które przez ostatnich kilka dekad zwróciły uwagę zarówno społeczeństwa, jak i naukowców. Dowiedziono, że substancje te ingerują w prawidłową pracę układu hormonalnego i zaburzają rozwój, reprodukcję, homeostazę i metabolizm żywych organizmów. Zagrażają nie tylko ludziom, ale także wszystkim żywym organizmom. Są obecne w: plastikach, między innymi plastikowych opakowaniach na żywność, detergentach, pestycydach, tworzywach ognioodpornych, metalach ciężkich, a także farmaceutykach i produktach codziennej higieny, takich jak kosmetyki - kremy czy mydła, filtry UV, doustne środki antykoncepcyjne i przeciwbólowe, a także w wielu innych produktach. Nie zawsze są wykryte i usunięte ze ścieków, a w ten sposób dostają się do środowiska i gospodarstw domowych wraz z bieżącą wodą. W celu eliminacji powyższych substancji zanieczyszczających muszą być użyte odpowiednie techniki oczyszczania ścieków.

**Słowa kluczowe:** związki modulujące pracę hormonów estrogenowych, farmaceutyki i produkty codziennej higieny, oczyszczanie ścieków