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## SOURCES OF ENDOCRINE-DISRUPTING COMPOUNDS AND THEIR MIGRATION TO THE ENVIRONMENT

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### ŹRÓDŁA ZWIĄZKÓW ZABURZAJĄCYCH FUNKCJONOWANIE UKŁADU HORMONALNEGO I ICH MIGRACJA W ŚRODOWISKU

#### **Abstract**

The aim of this article is to present issues related to the presence and pathways of bisphenol A emission and its migration to wastewater and the environment. Bisphenol A (BPA) is an organic compound mainly used in the production of plastics. It is classified as an endocrine disrupting compound (EDC) and should therefore not be emitted to the environment. This paper presents basic information on bisphenol A, its applications and potential sources of emission to the environment. A wide review of literature confirming the occurrence of bisphenol A in sewage, sediments, natural waters, drinking water and the atmosphere is performed. Effective wastewater treatment and neutralisation of bisphenol A in sewage sludge could partially reduce the levels of BPA pollution in the aquatic environment.

**Keywords:** bisphenol A (BPA), wastewater, water, sediments, air

#### **Streszczenie**

Celem artykułu jest przedstawienie zagadnień dotyczących obecności i źródeł występowania bisfenolu A w ściekach i środowisku. Bisfenol A (BPA) jest związkiem organicznym, stosowanym przede wszystkim do produkcji tworzyw sztucznych. Należy do związków wykazujących negatywne oddziaływanie na układ hormonalny (*endocrine disrupting compounds*, EDC), w związku z czym nie powinien być emitowany do środowiska naturalnego. W artykule przedstawiono podstawowe informacje dotyczące bisfenolu A oraz potencjalne źródła emisji tego związku do środowiska. Dokonano przeglądu literatury potwierdzającej obecność bisfenolu A w ściekach, osadach oraz wodach naturalnych. Efektywne oczyszczenie ścieków i neutralizacja bisfenolu A obecnego w osadach ściekowych pozwoliłoby na częściowe ograniczenie zanieczyszczenia środowiska naturalnego.

**Słowa kluczowe:** bisfenol A (BPA), ścieki, woda, osady, powietrze

## 1. Introduction

The presence of organic contaminants in the environment has been studied for many years. Pesticides, solvents, substances used in industry and, relatively recently, pharmaceuticals have also become one of the most discussed topics in this context in scientific publications worldwide. Another group of environmental pollutants are endocrine-disrupting compounds or chemicals (EDCs) which affect the endocrine (hormonal) systems of living organisms. These compounds are characterised by an extremely negative impact on the environment and human health at very low concentrations.

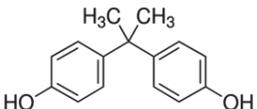
Natural and synthetic oestrogens have adverse effects on aquatic organisms at concentrations as small as 0.1 ng/l [24], they are toxic to humans and pose a risk through the consumption of fish and other animals living in water and exposed to these hormones. The other substance from the EDC group, bisphenol A, is a compound used on a very large scale and people are exposed to its harmful effects at work, in stores, on walks or even at home. Indirectly, logistics processes, such as transportation, waste disposal and management of waste are sources of environmental pollution from this compound.

The purpose of this paper is to present bisphenol A as a commonly occurring and harmful pollutant, its sources of emissions to the environment and the results of global research showing the presence of bisphenol A in wastewater, natural water, sediment and air samples.

## 2. Characteristic

Bisphenol A (BPA) is an organic chemical compound belonging to the phenol group. Its solid state is most commonly a white powder or flakes. It has a low level of solubility in water, but is soluble in metal hydroxides from alkali metal and organic solvents such as acetone, methanol, ethanol and diethyl ether. Table 1 presents basic information on BPA, such as molar mass, molecular formula and structure, and half-life in the human organism.

Table 1. Basic parameters of bisphenol A

Compound	Formula	Structure	Molecular mass [g/mol]	CAS no.
Bisphenol A (BPA)	$C_{15}H_{16}O_2$		228.29	80-05-7

The first method of preparation of BPA was its synthesis by two molecules of acetone and phenol in acidic conditions. This method was efficient (under the excess of phenol), and had an important advantage in the fact that the only by-product was water; however, the commercial production of BPA requires the large-scale distillation of a mixture of many by-products.

Bisphenol A is classified as an endocrine-disrupting substance which has a negative impact on the hormonal system of humans and animals mimicking the effect of female hormones (oestrogens); furthermore, the exposure of foetuses to BPA can trigger subsequent physical and neurological problems. It is also suspected of carcinogenicity and because of that, bisphenol A was classified as a compound which is extremely hazardous to humans and the environment.

### 3. Potential sources of emission

Figure 1 illustrates the potential sources of EDC (including BPA) release to the environment. Bisphenol A is widely used in the production of plastics, especially polycarbonate resins e.g. it is an essential monomer for epoxy resin. Such materials are used in the manufacture of a wide range of products, these include polycarbonate plastics, water bottles, baby bottles, sports equipment, CDs and DVDs, medical devices, dental sealants for teeth fillings, optical lenses and lining for water pipes. Epoxy resins containing BPA are used as linings for cans of food and beverages. Bisphenol A is also used as an antioxidant and an inhibitor in the production and processing of polyvinyl chloride, in the manufacture of car tyres, as flame retardant, in electronics, within the construction industry, in moulding and in the production of thermal paper for receipts [8]. This means that bisphenol A and materials produced with BPA are in widespread use in industrialised and developing countries.

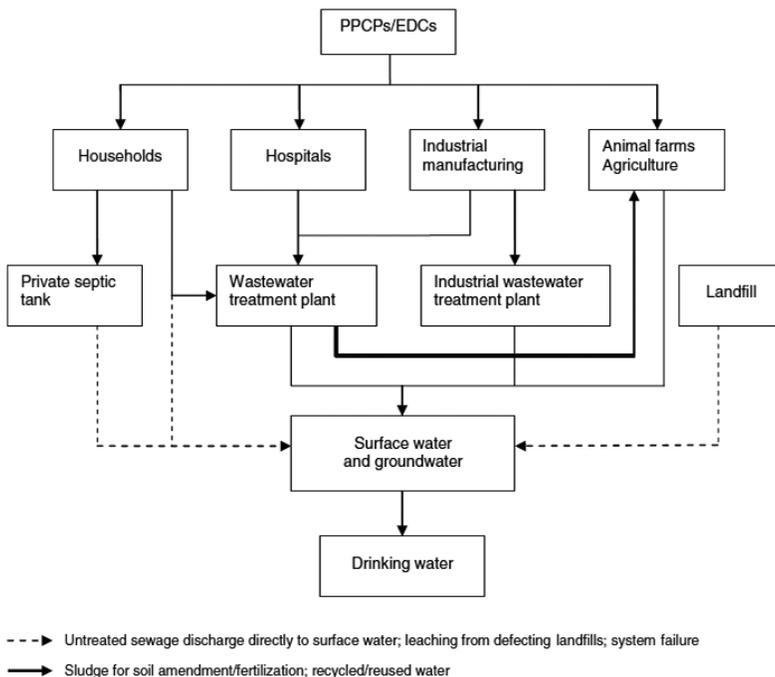


Fig. 1. Sources of endocrine-disrupting compounds (EDC) in the environment [7]

The main modes of human exposure to BPA are its ingestion, inhalation and contact with skin. Most BPA is ingested along with food, drinking water and beverages in cans and bottles, and tap water (due to the linings of water pipes containing BPA). Penetration into the body through skin may occur during normal use of products containing BPA, especially in the case of thermal paper receipts in which BPA is present in its free state (not in the form of polymer product) – this constitutes an increased risk of exposure to BPA for cashiers and customers. The penetration of bisphenol A into the body via inhalation may occur particularly while inhaling urban air polluted with BPA, being near a cash register during the printing of receipts and potentially during the recording of CDs and DVDs because the laser heats the plate to sometimes even up to 700°C. BPA is excreted primarily in urine, which is why household sewage is a significant source of BPA in raw wastewater within wastewater treatment plants [10].

The transportation, storage and disposal of waste containing BPA also poses a risk of environmental pollution. The presence of materials containing BPA in car tyres creates a continual risk of pollution through the abrasion of the tyres. Tyre particles may be blown into neighbouring roads and meadows and in the right conditions, it can also lead to BPA penetration into soil. Transportation or storage in landfills of inadequately protected materials that contain BPA also poses a risk of wastes spreading across the environment. Emissions to soil and groundwater can occur by eluting residues of BPA in precipitations from products containing it e.g. thermal paper. The combustion of materials containing bisphenol A also contributes to the pollution of the environment, in this case the atmosphere; however, the primary source of BPA in air samples is the production of BPA itself.

#### **4. Occurrence in the environment**

Bisphenol A present in the wastewater fed to the municipal wastewater stream comes mainly from wastewater produced in households and from industrial effluents that have been pre-screened and then discharged to the municipal treatment plant. Table 2 presents the confirmed cases of BPA detection in sewage treatment plants (raw and treated wastewater), natural waters and sewage sludge and sediments. Insufficient degradation or elimination of BPA during wastewater treatment processes results in the emission of BPA with the discharge of effluent into rivers or reservoirs and contamination of the aquatic environment.

The presence of BPA in the aqueous environment is not only related to effluent discharged from urban wastewater treatment, but also to pre-treated wastewater discharged directly from the factories and industrial wastewater treatment plants. If polluted wastewater is discharged into a body of water which is a tributary to other watercourses, bisphenol A will migrate and contaminate another river or even groundwater. The data reported in Table 2 confirms the ability of BPA to migrate into groundwater through, among other routes, permeable layers. BPA can also partially accumulate by passing through soil and river sediments.

Table 2. Concentrations (min-max or mean) in ng/l or ng/g dry mass for sediments of BPA; b.l.q. – below level of quantification

Influent	Effluent	Surface water	Groundwater	Sediments
13-2140 <sup>[15]</sup>	2-44 <sup>[43]</sup>	1.2-1900 <sup>[1]</sup>	b.l.q.-494 <sup>[17]</sup>	0.17-1.25 <sup>[2]</sup>
60-600 <sup>[43]</sup>	30-1100 <sup>[15]</sup>	2.1-87 <sup>[13]</sup>	b.l.q.-7000 <sup>[19]</sup>	0.58-36700 <sup>[8]</sup>
360-1620 <sup>[18]</sup>	35-86 <sup>[23]</sup>	2.2-4230 <sup>[21]</sup>	b.l.q.-9300 <sup>[28]</sup>	1.1-43 <sup>[42]</sup>
378-890 <sup>[9]</sup>	110-300 <sup>[18]</sup>	6-34 <sup>[23]</sup>	1-1136 <sup>[20]</sup>	4.3-130 <sup>[25]</sup>
416-2050 <sup>[23]</sup>	700 <sup>[40]</sup>	6-68 <sup>[11]</sup>	1-11 <sup>[4]</sup>	10-530 <sup>[23]</sup>
1800 <sup>[40]</sup>		6-500 <sup>[26]</sup>	79-2550 <sup>[15]</sup>	53-196 <sup>[43]</sup>
		6-881 <sup>[22]</sup>	600-11000 <sup>[14]</sup>	0.32 <sup>[6]</sup>
		7.5-334 <sup>[12]</sup>		
		55-162 <sup>[27]</sup>		
		192-215 <sup>[15]</sup>		
		460-4800 <sup>[25]</sup>		

Fu and Kawamura [5] showed that bisphenol A is also present in air samples. In the agricultural areas of China, its concentration in the air does not exceed 240 pg/m<sup>3</sup>, but the air samples in urban areas are more contaminated (20-2.340 pg/m<sup>3</sup>). Definitely, more air pollution bisphenol was found in India, where its concentration reached 9,820 and 17,400 pg/m<sup>3</sup>. Air samples collected in coastal areas around the world contain trace amounts of BPA that does not exceed 32 pg/m<sup>3</sup>. These results show how large the scale of bisphenol A pollution is in the environment – it is not only water that is contaminated but also the air and soil. Considering how large is the current need for BPA (despite attempts to withdraw from the production and use of bisphenol A in Canada), constantly increasing levels of environmental pollution can be expected.

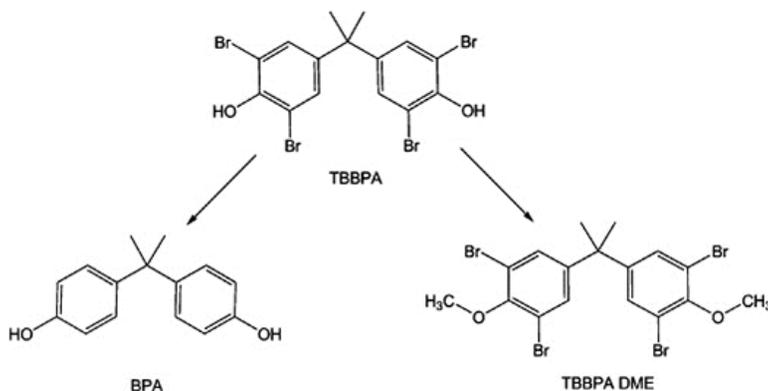


Fig. 2. Microbial-induced transformation of TBBPA to BPA and TBBPA DME [16]

It should be kept in mind that the presence of BPA in the environment can be linked not only with BPA itself, but also with more complex compounds that may transform into BPA. One of the most widely used brominated flame retardants, tetrabromobisphenol A (TBBPA) – depending on the conditions under the influence of bacteria present in the environment, this can be transformed into BPA (reductive debromination in anaerobic conditions),

TBBPA DME (dimethyl ether) and TBBPA monomethyl ether (O-methylation in aerobic conditions) (Fig. 2). This may explain the very high concentrations of BPA in groundwater (anaerobic conditions).

## 5. BPA in other matrixes

Previously mentioned data provides a picture of the wide migration of bisphenol A occurring in the aquatic environment. Bisphenol emitted to sewage or directly to surface water may accumulate in sewage sludge or river sediments; the use of such sludge for agricultural purposes may contribute to even greater levels of BPA pollution of soils.

If bisphenol A is present in the source water of a drinking water treatment plant, there is a risk that it can penetrate to the finished water despite the use of modern methods of treatment. There are known cases of bisphenol A detection in drinking water in China between 15-63 ng/l and 38.9-55.8 ng/l [8]; in Canada, 100 ng/l; in the USA, up to 24 ng/l [15]; also in other countries at concentrations not exceeding 100 ng/l (0.5-99 ng/l) [1].

Ingestion of drinking water polluted with bisphenol A is an additional route of exposure of the human body to BPA. Studies have shown that BPA was detected in the analysed samples of blood serum and urine at concentrations of 0-2,500 ng/l in serum and 110-3,200 ng/l in urine [41]. Also in Japan, BPA was detected in 23 samples of breast milk at concentrations of 280-970 ng/l [29]. This confirms the suspicion of the possibility of exposure of infants and young children to the harmful effects of BPA.

## 6. Conclusions

Bisphenol A is ubiquitous in the environment, not only in effluents and natural waters, but also in soil and the atmosphere. Its wide use hinders any control over the level and scale of pollution and calls into question any plans to withdraw the substance from production. Due to its advantages, in many countries bisphenol A is and will be the main raw material for the production of polycarbonate plastic used in the production of baby bottles. The first step should be the removal of BPA from everyday life where it is not needed and poses a direct threat to the body, especially for infants and young children (replacing linings in pipes and removing the material from the production of baby bottles). The next step should be to protect the air in workplaces (BPA withdrawal from the production of thermal paper) and areas adjacent to factories producing or using bisphenol A.

This does not mean that we need not care about the environment itself. Inefficient wastewater treatment and inadequate protection of landfill result in pollution of water and soil – this could ultimately mean exposure to human health through repeated contact with BPA. The application of membrane processes using reverse osmosis (RO) and nanofiltration (NF) could be used for efficient BPA removal. Experiments conducted by Dudziak and Bodzek [3] showed 85% and 70% reductions of bisphenol A from water solutions through

the use of RO and NF, respectively. Contaminated agricultural land (and consequently crop yields) and drinking water containing bisphenol A are additional sources of penetration of the harmful compound to the human body.

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