

BPA – an endocrine disrupting compound in water used for drinking purposes, a snapshot from South Poland

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Received: 19 December 2019; accepted: 10 February 2020; first published online: 20 February 2020

Abstract: Bisphenol A (BPA) is a chemical produced in large quantities for use primarily in the production of polycarbonate plastics and epoxy resins. As an endocrine disrupting compound, it has been included in the list of substances requiring special supervision as a very high-risk substance due to its toxic influence on reproduction. BPA with a reference value of 0.01 µg/L was included in the Drinking Water Directive revision (DWD 2018). This paper presents the results of preliminary studies aimed at identifying the occurrence of BPA in different types of water, i.e. groundwater captured with house wells or flowing wells in a selected location in southern Poland. These waters are commonly used as a source of water intended for human consumption and their quality is not regularly controlled. Additional tests were carried out for surface water, as well as water from springs used for drinking purposes. The authors also analysed tap water from various sources, i.e. surface and groundwater, as the final product of the drinking water production cycle.

The results indicate the presence of BPA in water and the necessity of a detailed study on the risk of the BPA occurring in groundwater, especially in domestic wells.

Keywords: emerging contaminants, endocrine disrupting compounds, groundwater protection, groundwater domestic wells, bisphenol A

INTRODUCTION

The increasing use of pharmaceuticals, both for humans and animals, also results in a growth in the concentration of endocrine disrupting compounds and products of their metabolism in sewage, and thus in surface water, groundwater (i.e. domestic

wells) and tap water, which are subsequently consumed by humans (Loos 2012, 2015). The seriousness of the problem is documented by the rich literature devoted to emerging contaminants (EC) and endocrine disrupting compounds (EDCs) in the aquatic environment, e.g.: Cunningham et al. (2006), Kümmerer (2009), Loos et al. (2010),

Snyder & Benotti (2010), Sanderson (2011), Kozisek et al. (2013), Rocha et al. (2013), Webb et al. (2013), Küster & Adler (2014), Schaidler et al. (2014), Corrales et al. (2015), Lin et al. (2015), Baranauskaitė-Fedorova et al. (2016), Clayton (2016), Paxéus et al. (2016), Yan et al. (2016), Bilal et al. (2018), Rasheed et al. (2019), Wazir & Mokbel (2019).

According WHO (2012) an endocrine disruptor “is an exogenous substance or mixture that alters function(s) of the endocrine system and consequently causes adverse health effects in an intact organism, or its progeny, or (sub)populations” and a potential endocrine disruptor “is an exogenous substance or mixture that possesses properties that might be expressed to lead to endocrine disruption in an intact organism, or its progeny, or (sub)populations”.

EDCs enter into the environment and groundwater through many routes: human or animal excreta, wastewater effluent, treated sewage sludge, industrial waste (also pharmaceutical), medical waste from health-care and veterinary facilities, landfill leachate, surface runoff biosolids, as well as indirectly through the process of groundwater-surface water exchange (Lapworth et al. 2012, WHO 2012). Groundwater, especially that from shallow aquifers, is intensively supplied by the infiltration of atmospheric precipitation. Precipitation transports different pollutants by washing dumping grounds, urban-industrial agglomerations, areas of crops, etc. Migration of these substances is a major threat to groundwater resources (Witczak et al. 2013). The domestic wells capturing shallow groundwater are most liable to pollution. EDCs and their metabolites undergo natural attenuation by adsorption, dilution or degradation in the environment, depending on their hydrophobicity, biodegradability and the temperature. Therefore, these compounds in water sources and drinking water are often present in trace concentrations, as they would have undergone metabolism and removal through natural processes and, if applicable, wastewater and drinking water treatment processes (WHO 2012).

The Water Framework Directive (WFD 2000) established a strategy for the prevention of water pollution covering i.a. identification of priority substances among those which represent a significant risk to the aquatic environment or through

it at the European Union level. In 2013, the European Commission introduced the obligation to draw up the so-called watch lists, covering such substances (EU 2013). Watch lists (EU 2015) concern only surface waters. The Groundwater Directive (GWD 2006) aims to prevent and combat groundwater pollution in the EU. In a document “Developing a groundwater watch list for substances of emerging concern: a European perspective” almost 280 compounds are considered as hazardous for humans, however, in most European countries only 31 of them were examined (Lapworth et al. 2019). Bisphenol A (with a limit reference value of 0.01 µg/L) was included in Part B of Annex 1 of the Drinking Water Directive revision (DWD 2018). This regulation will also be applied for groundwater, including domestic wells often used as a source of drinking water without regular quality control and treatment. The paper presents the results of preliminary studies aimed at identifying bisphenol A – an endocrine disrupting compound – in some sites in southern Poland.

Bisphenol A (BPA) is a chemical produced in large quantities for use primarily in the production of polycarbonate plastics and epoxy resins. It is mainly used in combination with other chemicals to manufacture plastics and resins (Pubchem 2017). It has been included in the list of substances requiring special supervision as a very high-risk substance due to its toxic influence on reproduction (ED/01/2017, ED/01/2018). Its endocrine disrupting activity is associated with cardiovascular disease, diabetes, obesity, and liver dysfunction (EU 2010).

BPA has been proven to have estrogenic activity even at concentrations below 1 ng/L (Rykowska & Wasiak 2006). The effects of exposure to BPA can be particularly harmful to i.a. infants and young children because of a lack of feedback regulating the activity, synthesis, and elimination of hormones (Rykowska & Wasiak 2006, Careghini et al. 2015).

Endocrine disrupting compounds are more widely determined in water bodies. However, it turns out that EDCs, like alkylphenols and bisphenol A, are emitted into the atmosphere during fuel combustion, mainly because of technical reasons (since many domestic stoves are defective) and economic ones (since in many cases waste combustion is much cheaper than burning ecological fuel)

(Alliot et al. 2014, Lyons et al. 2014, Vorkamp et al. 2014, Salgueiro-González et al. 2015). Many studies have been conducted on BPA in soil and aquatic environments as well as the widespread and continuous human exposure to bisphenol through food, drinking water, dental sealants, cell phones and inhalation of indoor dust (Wilson et al. 2001, Rudel et al. 2003, Vandenberg et al. 2007, Fu & Kawamura 2010). Bisphenol A is not likely to occur in the gas phase of the atmosphere as its vapor pressure is very low. But as atmospheric releases of bisphenol are reported during production, an association with aerosols particulates is possible. Bisphenol has attracted considerable public attention due to its potential association with adverse health effects such as prostate cancer, obesity, neurobehavioral and reproductive problems (Krishnan et al. 1993, Vogel 2009, Fu & Kawamura 2010). BPA was detected in 40% of groundwater bodies identified as drinking water sources investigated in Europe (Loos et al. 2010, Arnold et al. 2013, Postigo & Barceló 2015).

The achievements of Polish researchers on the scope of this form of pollution as an emerging group of contaminants are significant. Literature studies of the occurrence of the pharmaceuticals, EDCs and their residues in Poland have focused mainly on sewage, surface water, and water intended for human consumption. However, there is little information about groundwater pollution caused by these substances. A comprehensive study on the occurrence, removal, mass loading, and environmental risk assessment of 19 multi-class emerging organic contaminants (i.a. bisphenol A) in groundwater from two MSW landfill sites located in northeast Poland is presented in Kapelewska et al. (2018). BPA was found in all of the analyzed samples. Its concentrations in groundwater were at the level of <0.003 – 6.88 $\mu\text{g/L}$. In 2016 Polish Geological Institute-National Research Institute (PGI-NRI) conducted pilot studies on the amounts of the pharmaceuticals in groundwater in Poland (Kuczyńska 2017). Among the analyzed parameters were compounds belonging to the group of endocrine disruptors, i.e. estrone, estriol, 17- α -ethinylestradiol, 17- β -estradiol, but they were found only in selected areas. BPA was not analyzed during this research study. Preliminary results of the pharmaceutical

residues in the groundwater of southern Poland were presented by the authors of the work at several worldwide conferences (Kmieciak et al. 2017a, 2017b, 2018, Wątor et al. 2017).

In this paper, the results of simple tests are presented. The aim of the research was the determination of the occurrence of BPAs in different kinds of water which are used for drinking purposes. Also, samples of total amounts of BPAs suspended in air particles and soils were tested to indicate possible routes of BPA migration in the environment.

MATERIALS AND METHODS

During the first sampling campaign (in February 2017) grab water samples were collected. The location of sampling points is presented in Figure 1.

Samples of water intended for human consumption were collected from taps from different sources (surface water, groundwater and domestic wells in the vicinity of agricultural areas) (Tab. 1 on the interleaf). The samples of flowing surface water (rivers) and groundwater (wells and spring) were also taken from areas where they are used for drinking purposes.

Water samples were collected in accordance with the procedures given in the 5667 series ISO standards (*Water quality – Sampling*) and transferred into 500 mL glass bottles. Samples were stored in a fridge and transported to the laboratory in a short time (a few hours).

Solid phase extraction (SPE) was used for the extraction of the BPA from the aqueous samples. SPE was carried out with a System BAKER spe 12G. Oasis HLB extraction cartridges were conditioned with CH_3OH (2 mL) and H_2O (2 mL). Samples (1 L) were spiked with 200 ng of internal standard (bisphenolA-D16) and then passed through the HLB cartridge at a rate of 6 mL/min. After the extraction was completed, the cartridges were dried under full vacuum for 20 min. The elution was performed using 4 mL of CH_3OH . The extracts were dried to dryness under argon at 35°C and then dissolved in 200 μL of derivatization reagent. The silylation process with BSTFA+1% TMCS was carried out at 65°C for 35 min in a thermo-block. Solutions were then analyzed by GC-MS/MS (Nosek et al. 2014).

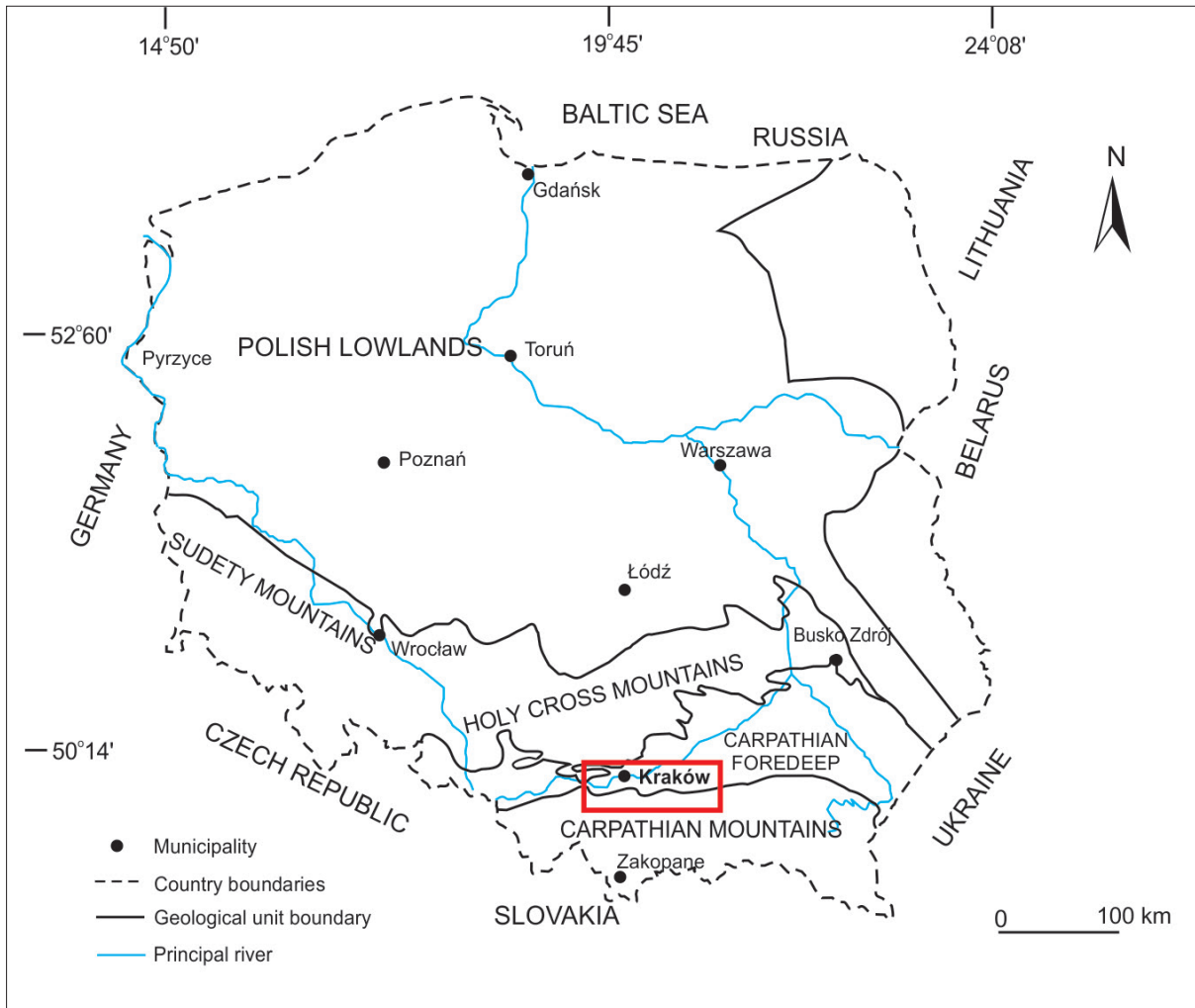


Fig. 1. Location of sampling points P1–P8

Table 1
Characteristic of sampling sites and summary of sampling series

Sampling point Id	Kind of water	Characteristics	Sampling series		
			1 st (II 2017)	2 nd (XI 2017)	3 rd (II 2018)
P1	surface water	The stream flows parallel to the road, between houses and farms where not all farms are connected to the sewage system (cesspool), farmlands and numerous forest areas are found around the farms	water (glass containers)	–	–
P2		It flows between the houses and farms through the areas where not all of the farms are connected to the sewage system (cesspool) and near to the farmlands		water (plastic container)	water (plastic and glass container)
P3	spring/ground-water	The spring flows from the slope of the mountain, the intake is enclosed by stone slabs, water flows in a continuous stream along a rocky grove, forest areas are mostly found around as well as farmlands, farms and house where not all farms are connected to the sewage system (cesspool). The water is a source of drinking water for residents		water (plastic container) soil	–
P4	ground-water	Domestic well, connection at home, galvanized steel pipes, 30-year-old installation, the well is located about 50 km from the bank of river P2		water (plastic container) soil air	water (plastic container)
P5		Domestic well, the connection at home, galvanized steel pipes, 30-year-old installation		water (plastic container)	–
P6	tap water	Treated surface water, central installation which is about 60-year-old, 5-year-old installation at home, plastic and steel		–	–
P7		Treated surface water, central installation is about 15-year-old, 15-year-old installation at home, plastic and steel		–	–
P8		Groundwater intake, central installation which is about 20-year-old, 1-year-old installation at home, steel		–	–

The analysis was carried out with the usage of Thermo Scientific GC Trace 1300 gas chromatography coupled to a ITQ 900 ion trap mass spectrometer and a TriPlus RSH autosampler. The flow of helium through a GC column was constant and set at 1 mL/min. The programmable temperature of the vaporization injector was maintained at 250°C, the transfer line at 250°C and the ion source at 250°C. The injector was operated at splitless conditions for 2 min. The volume of injections was 1 µL. All the compound separations were performed on a TG-SQC capillary column from Thermo Scientific that had a 30 m × 0.25 mm inner diameter and a film thickness of 0.25 µm (5% phenyl 95% dimethylpolysiloxane). The temperature program was as follows: 70°C for 2 min, from 70 to 320°C at 20°C min⁻¹, and finally 5 min at 320°C. The analyses

were performed in a positive mode, an electron energy 70 eV and emission current 250 µA. Helium (99.999%) was used as a collision gas with a flow of 0.3 mL/min. Mass spectrometry analyses were performed in the multiple reaction monitoring (MRM) mode measuring the fragmentation of the precursor ions. Data was collected, analyzed and processed using a Thermo Xcalibur. Limits of detection and quantification were calculated based on signal to noise ratios (S/N) of 3 and 10, respectively (Tab. 2). Deuterated internal standard (bisphenol A-D16) was added before SPE extraction to compensate for losses or enhancement of compounds during both the sample preparation procedure and resulting from matrix effects. The correlation coefficient (r^2) of the calibration curve was 0.9987 for the concentration range studied (0–500 ng/mL).

Table 2

GC-MS/MS method parameters for the analysis of BPA (calculated during method validation)

Retention time [min]	m/z for characteristic ions (for quantification)	Method detection limit MDL [ng/L]	Method quantification limit MQL [ng/L]
13.37	357 → 191,267	0.15	0.5

The recovery of BPA was 88%. The estimated measurement uncertainty is 30% (Kmieciak et al. 2018). During the second series (November 2017) water samples from selected points were collected where the highest BPA concentrations were observed in the first series (P2–P5).

In parallel, **soil samples** from the investigated areas were also taken (points P3, P4). Topsoil samples from the depth 0–20 cm (about 10 primary samples) were placed in a container from randomly selected points around the well/spring using an Egner's stick. All primary samples were mixed and averaged, and a bulk sample of approximately 0.5 kg was separated. Such collected samples were immediately delivered to the laboratory in a string bag. Soil samples were frozen and dried by lyophilisation, sieved through a 2 mm sieve and stored at 4°C until analysis. Dried soil samples of 5 g were spiked with 100 ng of BPA D16 and extracted with 10 mL of methanol for 1 h using horizontal shaker at 50 rpm, and centrifuged. The final extracts were evaporated to dryness and reconstituted in 100 µL of BSTFA+1% TMCS and derivatized at 65°C for 35 min. The recovery of BPA was 61%. The estimated measurement uncertainty is 19%.

From point (P4), an additional sample of the **total suspended in the air particles** (TSP) was collected. A low volume sampler was equipped with a filter holder, needle valve, membrane pumps and gas meters. The sampler worked with an air flow of 1.4 m³/h. Samples were collected on quartz fibre filters (Pallflex, Pall Life Sciences) with a 47 mm diameter. Before sampling, the filters were thermally pre-cleaned at 550°C for 5 h, cooled and equilibrated to constant humidity. Two samples of TSP were collected, in 70 h. The sampled filters were equilibrated for 24 h to achieve conditions comparable with the conditions of the weighing of empty filters. The mass of the particulate matter was obtained as an average of the three subsequent weighing results of each filter. The OHAUS Discovery DV215CD balance with an accuracy of ±0.01 mg was used for

weighing. The circular filter aliquots with a diameter of 22 mm were cut from the filters and then spiked with 10 µL (10 ng/µL) BPA D16 solution, after that extracted twice with 3 mL dichloromethane and 2 mL cyclohexane, for 40 min. The volume of combined extracts was reduced to 250 µL, using a gentle stream of argon at 35°C. The 100 µL of concentrate was finally transferred into the chromatographic vial, derivatized with BSTFA+1% TMCS (65°C, 35 min) and analyzed with GC-MS/MS. The recovery of BPA was 67%.

During the third series of samples collection (February 2018), water samples from points P2 and P4 were collected. In the case of P2, they were placed in plastic (p – BPA free) and glass (g) containers.

RESULTS AND DISCUSSION

Bisphenol A was found in all samples tested during the 1st series (Fig. 2). Their concentrations range from 6 ng/L (P7) through 351–427 ng/L in surface water (P1, P2) to 629 ng/L in spring water (P3). The lower concentration of bisphenol A in the tap water (P6–P8 – 6–53 ng/L) confirms their removal during the water treatment process. The highest concentrations of bisphenol A were found in the sample of spring water (P3 – 629 ng/L) and groundwater from domestic wells (P4 – 518 ng/L, P5 – 255 ng/L) located in villages where the sewage system is not very common and surface runoff is possible. BPA concentrations in all samples except P7 exceed the maximum permissible limit sets in the drinking water directive (DWD 2018).

Bisphenol A was one of the most relevant compounds detected in European groundwater described in the study of Loos et al. (2010) (autumn sampling series, the maximum measured concentration of BPA 2.3 µg/L). In groundwater, higher BPA concentration levels were also observed than in surface water. Environmentally significant concentrations of EDCs are being detected in

groundwater globally (Lapworth et al. 2012) but concentrations of these compounds change over time. The data from the literature indicate that the highest concentrations are observed in winter (Daneshvar et al. 2010, Baker & Kasprzyk-Hordern 2013, Boleda et al. 2013, Paxéus et al. 2016, Petrie et al. 2016). The results of the first series concern only the instantaneous concentrations of bisphenol A in single water samples collected in February and therefore may be higher than in other seasons. It may be related to rainfall, temperature, etc. What is more, this series of samples was collected during the height of the heating season, after several months of the intensive combustion of various fuels in domestic boiler rooms, which may affect the results obtained for the determination of bisphenol A. Therefore, at the beginning of the heating season in November 2017, a second series of tests was carried out. Samples were collected in plastic containers (BPA free) from those points in which high concentrations of bisphenol A had been found in February (P2–P5). In parallel, soil samples were also taken (points P3, P4)

and from point (P4) an additional sample of the total suspended in the air particles was collected. The results for water samples are also presented in Figure 2. This time, BPA concentrations in the surface water sample (P2) and groundwater samples (P3–P5) were at a very low level, about 1 ng/L.

In the soil samples, BPA was determined at the level of 4 ng/g (P4) and 10 ng/g (P3). In the literature, there is only a little information about BPA in soil samples. For example, researchers have proven that the contamination of industrial soil with BPA was higher (mean concentration 11.28 ng/g) than for agricultural soil (mean concentration 2.42 ng/g) (Sánchez-Brunete et al. 2009, Fischer et al. 2014). BPA concentrations for landfill soil ranged from <0.1 to 2.8 ng/g (Hansen & Lassen 2008, Sánchez-Brunete et al. 2009, Fischer et al. 2014). The results of the analysis performed for soil samples at points P3 and P4 are relatively high. Research provided by Styszko (2016) indicated that bisphenol A had relatively poor sorption properties which were dependent on the type of sediments/soils.

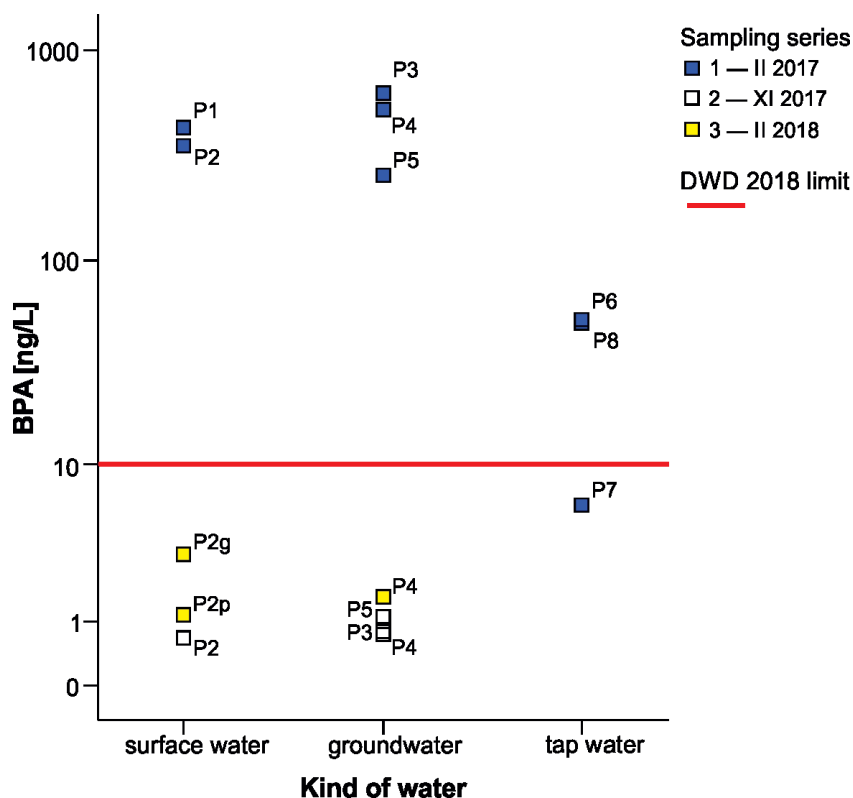


Fig. 2. The results of bisphenol A determination in the analyzed samples

In the sample of air particulate matter from point P4, 2.83 ng/m³ of BPA was determined. Fu & Kawamura (2010) showed that in the agricultural areas of China, BPA concentration in the air does not exceed 0.240 ng/m³, while in urban areas it reaches concentrations ranging from 0.020 to 2.340 ng/m³ (Kryłów & Rezka 2017). A positive correlation was found in urban regions between BPA and 1,3,5-triphenylbenzene, a tracer for the burning of plastic, indicating that the open burning of plastics in domestic waste should be a significant emission source of atmospheric BPA (Fu & Kawamura 2010). The concentration of BPA in the air particulate matter from point P4 suggests that one of the possible sources of this compound in the investigated areas, where neither industry nor high traffic occurs, is the burning of plastics in domestic waste. From the air, BPA can migrate to the soils and water – surface and groundwater.

During the third series of sampling (February 2018) samples from points P2 and P4 were collected. In the case of P2, these were placed in plastic (p – BPA free) and glass (g) containers. BPA was identified in all samples, also in small concentrations (Fig. 2), but higher than in the second series. In sample P4, BPA was measured at the level 1.61 ± 0.37 ng/L. There was a difference in BPA determination in sample P2 from the plastic (1.13 ± 0.17 ng/L) and glass containers (3.17 ± 0.92 ng/L), probably occurring during the sorption processes. The research will be expanded to explain the behavior of BPA under different conditions. Column and batch experiments are planned (Okońska & Pietrewicz 2018, Okońska et al. 2019a, 2019b, 2019c).

In 2015, the European Food Safety Authority reduced the tolerable daily intake (TDI) for BPA from 50 to 4 µg/kg BW/day. TDI is “the maximum amount of a substance to which any individual can be exposed every day of his/her life, through all possible sources, without any risk to his/her health” (EFSA 2019). Maximum Allowable Dose Level (MADL) is the exposure level at which a chemical would have no observable reproductive effect even if a person were exposed to 1000 times that level. Goodman et al. (2017) estimated this parameter at the level of 157 µg/day. Drinking water equivalent level (DWEL, µg/L) can be

calculated from TDI, multiplying by the default adult body weight (about 70 kg) and divided by average daily water consumption (2 L):

$$\begin{aligned} \text{DWEL} &= 4 \mu\text{g/kg BW/day} \times 70 \text{ kg BW} / 2 \text{ L} = \\ &= 140 \mu\text{g/L}. \end{aligned}$$

In the Health Based Guidance for Water Health Risk Assessment Unit (MDH 2015) there are other BPA limits:

- Short-term Non-Cancer Health Risk Limit (nHRLShort-term) = 100 µg/L,
- Subchronic Non-Cancer Health Risk Limit (nHRLSubchronic) = 20 µg/L,
- Chronic Non-Cancer Health Risk Limit (nHRLChronic) = nHRLSubchronic = 20 µg/L.

The concentrations of BPA observed in the analyzed samples are lower than the above limits, therefore they do not pose a threat to the health of the people drinking this water.

CONCLUSIONS

Pollution of the environment by means of endocrine disrupting substances is an emerging problem. There is a lack of knowledge about the presence of many of them in the environment (i.a. in groundwater) and about the levels that could be harmful for human health. The main goal of the presented preliminary research was to identify the risk from exposure to BPA – an important endocrine disrupting compound – through consumption of drinking water from different sources, including groundwater from house (private) wells. These wells take water from Quaternary formations, so they are most exposed to contamination, also by EDCs. The problem is that the quality of groundwater taken from small domestic wells is not controlled and, even if it is, EDCs are not determined.

As the results of the conducted research show, BPA occurs in shallow groundwater in Poland, including water captured by small domestic wells. There is a need for regular research on the scope of the presence of BPA in groundwater. Meanwhile, the lack of analytical procedures constitutes a limitation to the reliable quantification of EDCs in groundwater, especially those occurring in very low concentrations, and affects the estimation of

human exposure to the discussed pollutants. Although studies and reviews can be found in the literature on sources, occurrence, environmental behavior, and the fate of BPA, the pathway of this pollutant from sources to receptors should be subject to advanced research. This is because the information is still insufficient, mainly due to the complexity of the environmental systems which may determine an unexpected behavior of the BPA in the air, water, or soil. The consequences of BPA in aquatic ecosystems are of particular concern since living organisms are subjected to exposure, with potential consequences for future generations.

The research presented in this paper is ongoing. Samples are being collected with different frequencies, allowing us to determine the trends/fluctuations of bisphenol in groundwater used for human consumption. The presented preliminary results indicated that there are changes in BPA concentrations during the course of a year. The influence of weather conditions such as precipitation, wind or temperature should be taken into account during the interpretation of results. The use of passive sampling or collection of composite samples (daily/week), column and batch experiments can give more reliable results which will help to identify the migration routes of bisphenol A into the tested groundwater.

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