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Determination of phenolic compounds in surface waters using high-performance liquid chromatography and molecularly imprinted solid-phase extraction

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ABSTRACT

An effective and reliable analytical method based on molecularly imprinted solid-phase extraction (MI-SPE) and high-performance liquid chromatography with photodiode array detector was developed to simultaneously determine four phenolic compounds: bisphenol A, 2-phenylphenol, *tert*-octylphenol and nonylphenol. A molecularly imprinted polymer that can selectively recognize bisphenol A and alkylphenols was developed. A bulk polymerization method using bisphenol A as a template, acrylamide as functional monomer, ethylene glycol dimethacrylate as the cross-linking agent, acetonitrile as porogenic solvent and 1,1′-azobis(cyclohexanecarbonitrile) as initiator was applied. This polymer was applied for isolation and preconcentration of these phenolic compounds from surface water's sample of Opole Region (Odra River, Nysa Kłodzka River, Mała Panew River and Turawa Lake). Bisphenol A and 2-phenylphenol were found in all water samples. Concentration of these compounds ranged 0.011–1.046 µg/mL and 0.020–0.410 µg/mL, respectively. Nonylphenol and *tert*-octylphenol were not detected in any samples.

Keywords: Molecularly imprinted polymers; Solid-phase extraction; Bisphenol A; Alkylphenols; Surface water samples

1. Introduction

A variety of phenolic compounds are widely used in industry, agriculture and household. Phenol is used in the production of adhesives, phenol-formaldehyde resins, disinfectants, pesticides and dyes. These compounds also find application in the plastic and metallurgical industry. At the same time, bisphenol A is an important intermediate in the industrial manufacture of polycarbonate plastic, epoxy and phenolic resins, polyesters and polyethers. It is also used as an antioxidant in adhesives and printing inks. Materials containing bisphenol A (BPA) have a lot of applications. Therefore, this compound can be found in baby bottles, plastic food containers, tin cans, microwave dishes, toys, dental fillings, medical equipment and in many other products [1–3].

BPA and alkylphenols (APs) are presented in the environment in trace amounts: these phenolic compounds occur in surface and tap water, wastewaters, soil, dust and food [4–9]. These substances, due to their toxicity and widespread presence in the environment, pose a threat to the life and health of organisms. They affect the functioning of the immune system, reproductive system, thyroid negatively and contribute to the development of cancer (breast, ovarian, prostate and brain cancer). In recent years, it is ever more evidence that shows that some phenolic compounds

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affect adversely on the endocrine and reproductive system. Bisphenol A, alkylphenols and their derivatives are known and suspected endocrine-disrupting compounds (EDCs) that can mimic the body's hormones or interfering with the action of endogenous gonadal steroid hormones. These substances can cause infertility, endometriosis and abnormalities in the structure and functioning of the reproductive system (hypospadias, cryptorchidism). For BPA, the negative reproductive effect was observed for the first time in the early XX century. Both in vitro and in vivo studies reported the ability of bisphenol A to disrupt thyroid function through multiple mechanisms [10,11].

Globally, most natural and synthetic estrogens in the aquatic environments are in the low ng/L range. At the same time, industrial compounds, like bisphenol A or alkylphenols, are present in the μg to low mg/L range. Although it was used in various industries for many years, recent studies demonstrate that bisphenol A is harmful. BPA is released into the environment and food from plastic consumer products due to hydrolysis of the ester bond [12]. The U.S. Environmental Protection Agency considered that the maximum safe dose of BPA is 50 mg/kg b.w./d. Although the affinity of bisphenol A to estrogen receptors is 10–100 thousand times weaker than estradiol, many studies have shown its biological activity. It is a very weak xenoestrogen, but it shows a broad spectrum of activity. It can cause neurochemical changes in the brain, interfere with hormone production and precocious puberty. An animal and *in vitro* studies show that endocrine-disrupting chemicals affect hormone-dependent pathways responsible for male and female gonadal development. This influence can cause male and/or female reproduction system disorders, such as fertility, endometriosis, breast cancer, testicular cancer or poor sperm quality [13]. The negative reproductive impact in vertebrates, like fish, is manifested by overexpression of egg yolk protein precursor – vitellogenin. Therefore, it is used as a biomarker of active endocrine substances [14].

Whereas alkylphenols and their derivatives are released mainly into the aquatic environment from industrial and agricultural sludge. The concentration of nonylphenol and polyethoxylated nonylphenols in wastewater (Michigan) was set at 0.017–37 ug/L and 332 ug/L, respectively [15]. There is concern that these substances can accumulate in the tissues and interfere with the hormonal system.

Phenolic endocrine-disrupting compounds exist in the environment at very low concentrations together with other exogenous interferences. Therefore, it is necessary to develop simple, reliable and effective methods for isolation, preconcentration and sample clean-up of bisphenol A, alkylphenols and their derivatives from real samples (i.e., surface water samples, tap water, wastewaters, sewage effluents, etc.) [16–18]. For this purpose, solid-phase extraction is a routine method for extracting analytes from complex samples. This technique has many advantages: ease of operation, high recoveries, low consumption of organic solvent and a wide spectrum of stationary phases. However, this method isn't selective because it's based on nonselective interaction between compounds and stationary phases. Molecularly imprinted polymers (MIP) is an excellent alternative to conventional sorbents due to their selective recognition of target molecules. The MIPs are formed during copolymerization of functional monomers and cross-linking agents in the presence of the target molecule. Monomers bind these imprint molecules with hydrogen bonds, electrostatic interaction or hydrophobic interactions. Their functional groups are held in position by a highly cross-linked polymeric backbone. Removal of target molecule exhibits binding sites which are complementary in size and shape to imprint substance and other substances which have analogous structures.

Molecularly imprinted polymers have been already used for isolation, preconcentration and sample clean-up of bisphenol A nd other related compounds (e.g., bisphenol F, nitrophenols, chlorophenols) from food samples [4,19], urine [4], serum [4] and river water's sample [6,20–26].

The results, which were obtained during the previous experiments, clearly demonstrated that molecularly imprinted polymers show high recovery and good selectivity for phenolic compounds. Therefore, selected MIP was used for monitoring the presence of bisphenol A and alkylphenol in surface waters samples from the Opole Region during the year.

2. Experimental

2.1. Materials

Chemical standards of phenolic compounds: bisphenol A (BPA) (purity > 99%), 2-phenylphenol (2-PP) (>99%), *tert*-octylphenol (*t*-OP) (>97%) and nonylphenol (NP) (>94%, mixture of isomers) were from Sigma-Aldrich. The structure and basic information of BPA and alkylphenols are summarized in Table 1. Reagents for MIPs synthesis were acrylamide (AA), ethylene glycol dimethacrylate (EGDMA) (>98%, contains 90–100 monomethyl ether hydroquinone as inhibitor), 1,1′-azobis(cyclohexanecarbonitryle) and acetonitrile (HPLC grade) and were obtained from Sigma-Aldrich, except for acrylamide which Fluka supplied. All other solvents were purchased from POCH and were of analytical grade. Water was purified using a Milli-Q system from Millipore (Bedford, MA, USA).

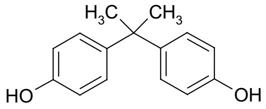
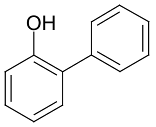
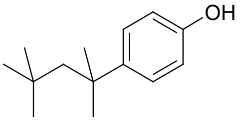
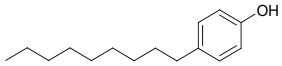
The standard solution of all phenolic compounds was prepared at a concentration of 1mg/mL in methanol and stored at 4°C in the dark.

Empty filtration tubes (volume 12 mL) and Teflon frits for solid-phase extraction (SPE) were obtained by Supelco.

2.2. Instrumentation

High-performance liquid chromatography (HPLC) analyses were performed using Dionex Ultimate 3000 with Photodiode Array Detector (FAD) operating at 225 nm. All phenolic compounds were analyzed using Microsorb-MV 100-5 octadecylsilane column (150 × 4.6 mm) with pre-column (MetaGuard 4.6 mm monoChrom 5 μm, C18). The mobile phase was a mixture of acetonitrile and ultrapure water. The mobile phase was pumped at a flow rate of 1 mL/min. The inject samples volume was 20 μL. The chromatographic separation was carried out using a multi-step gradient. The following method was used: 0 min. (50% A: 50% B), 0–5 min (65% A: 35% B), 5–15 min. (95% A: 5%B), 15–30 min. (95% A: 5% B), 30–35 min. (65% A: 35% B), 35–40 min. (95% A: 5% B).

Table 1
Structure and properties of the selected phenolic compounds in this study

Compound	CAS No.	Formula molecular weight	LogK_{ow}	Aqueous solubility (mg/L)	Structure	References
Bisphenol A	80-05-7	$C_{15}H_{16}O_2$ 228.3 g/mol	3.84	120		[15,16,18]
2-Phenylphenol	90-43-7	$C_{12}H_{10}O$ 170.2 g/mol	3.3	700		[17]
t-Octylphenol	140-6-9	$C_{14}H_{22}O$ 206.3 g/mol	4.1	12.6		[18]
Nonylphenol	84852-15-3	$C_{15}H_{24}O$ 220.4 g/mol	4.5	5		[18]

2.3. Sampling area

Opole Region is located in the south-western part of Poland between the two large agglomerations: Upper Silesia and Lower Silesia, and covers an area of 9412 km^2. This region is an industrial and agriculture area, where the development of agriculture conductive favourable climatic and soil conditions. Also a highly developed industry, mainly machinery, chemical, mineral, timber, textile and steel industry is presented on this area.

The main river in Opole Region is the Odra River. The other larger rivers are Nysa Kłodzka River and Mała Panew River, which are tributaries of Odra River. The largest lakes are artificial reservoirs, such as Nyskie Lake, Otmuchowskie Lake and Turawa Lake.

2.4. Real water samples

Surface water's samples were obtained from Odra River, Nysa Kłodzka River, Mała Panew River and Turawa Lake of Opole Region. They were taken from July 2017 to June 2018 of every month, except January (experiment I) and subsequently water's samples from Turawa Lake and Mała Panew River (upstream and downstream of the lake) from October 2018 to January 2019 (experiment II). The primary location information is presented in Fig. 1. All the samples were collected from a depth of about 30–50 cm below the water table. Samples were taken in triplicate of volume 500 mL and then mixed to obtain the average sample, which was studied. The distance between each sample collection site was about 200 meters. To avoid contamination of bisphenol A and its derivatives only glass bottles are used. These bottles were previously thoroughly washed, rinsed with ultrapure water and later, on-site, with a water sample.

Surface water samples were filtered through filter paper to remove particulate matter. Conductivity and pH were measured using multifunction devices (CX-501, Elmetron, Poland). All samples were stored in a refrigerator at 4°C before extraction.

2.5. Preparation of MIP by bulk polymerization

The non-covalent approach was used to prepared a molecularly imprinted polymer (MIP). The MIPs synthesis protocol has been previously in detail described [27].

Briefly, template (BPA; 0.25 mmol), functional monomer (AA; 4mmol), crosslinking agent (EGDMA; 20 mmol), acetonitryle (20 mL) as porogenic solvent and 1,1′-azobis (cyclohexanecarbonitrile) as initiator was used.

The obtained polymer was washed with several aliquots of methanol until no BPA could be detected in the supernatant solution by HPLC-DAD. Afterwards, it was used as sorbents for SPE.

2.6. MI-SPE method

In this study, solid-phase extraction was performed using a 12-position manifold device (Merck) with a membrane vacuum pump (Vacuubrand).

Four hundred milligrams of dry particles of the molecularly imprinted polymer was packed into an empty 12 mL polypropylene SPE tube and were subsequently capped with the Teflon frits at the top and bottom to form a regular sorbent bed.

The results are presented as recovery, defined as the compound percentage after extraction relative to the initial amount.

The MIP was evaluated as SPE sorbent using standard water solution at a concentration of 0.02 µg/mL of each

Fig. 1. Area map of Opole Region with the sampling locations.

analyte to find the optimum conditions. Different mixtures of methanol/water/acetic acid (95: 2.5: 2.5; v:v:v) were tested as washing and elution solvent. Elution with 5 mL of this mixture resulted in high recoveries: from 103% for BPA to 53% for NP and good repeatability (RDS < 6%).

Firstly column was conditioned with 10 mL of methanol and 10 mL of water. The natural water samples (250 mL) was adjusted to pH 5.5 by adding hydrochloric acid and was loaded onto the column filled with the polymer at a flow rate of approximately 2 mL min^{-1}. After the sample loading, the column was washed with 1.5 mL of methanol/water/acetic acid (95: 2.5: 2.5; v:v:v). Finally, the analytes were eluted with 5 mL of mixture methanol/water/acetic acid.

Before SPE experiments, the cartridges were first washed with 10 mL of methanol to remove possible residues from previous extraction and next conditioned with methanol (10 mL) and water (10 mL).

All samples were analyzed using high-performance liquid chromatography (HPLC).

2.7. Limit of detection and limit of quantification

Limit of detection (LOD) and limit of quantification (LOQ) for all analyzed phenolic compounds were designated using the graphical method. The analytes were determined in spiked water samples for three concentration levels in the range of 0.1–1 µg/mL for BPA, 2-PP, *t*-OP or 1–10 µg/mL for NP (n = 5). For each series of measurements were calculated by standard deviation S and plotted the graph of function $S = f(c)$. LOD was defined as $3s_0$, where s_0 is intercept values. LOQ for each compound was calculated as 3 LOD.

Values of calibration equations, coefficients of correlation (r^2) for the standard solution of phenolic compounds and limit of detection and limit of quantification spiked real water's samples are presented in Table 2.

3. Results and discussion

Based on the previously obtained results [27], MIP with acrylamide as a functional monomer was selected to simultaneously extract endocrine phenolic compounds (bisphenol A, 2-phenylphenol, *t*-octylphenol and nonylphenol). In the first stage, MIP was used to extract the aqueous solution with a concentration of 0.02 ug/mL of each compound and a volume of 250 mL. The extraction was performed according to the previously described procedure, using a mixture of methanol: acetic acid: water (95:2.5:2.5) as an eluent. This sorbent was characterized by high recovery values of the tested compounds: 104% BPA, 103.2% of 2-PP, 75.6% of *t*-OP and 53.7% of NP (RDS < 6%). The results indicated the possibility of application of molecularly imprinted polymer for extraction of analytes from real water's samples.

3.1. Characteristic of surface waters samples

The samples were from surface waters of three rivers (Odra River, Nysa Kłodzka River and Mała Panew River) and one lake (Turawa Lake) located in the Opole Region. Nysa Kłodzka River and Mała Panew River are tributaries of Odra River, whereas Turawa Lake is a storage reservoir built on Mała Panew River. These surface waters are heavily polluted due to the high industrialization of the region and the presence of large areas of agricultural land.

The waters samples had a pH ranging from neutral to slightly alkaline, taking values from 6.93 to 8.37. The values of conductivity were between 222 and 596 µS for Nysa Kłodzka River, Mała Panew River and Turawa Lake. Whereas for the Odra River, conductivity values were much higher and more differential –from 346 to 1,546 µS. The changes in pH and conductivity during the year are shown in Fig. 3.

3.2. Matrix effect – influence of conductivity

The values of recovery of BPA and alkylphenols for the standard water samples at the concentration of 0.02 µg/mL (pH = 5.5, conductivity = 2.036 µS) were determined, obtaining good results. Analogous studied were performed for real spiked samples (pH = 5.5 by adding a few drops of hydrochloric acid) containing 0.02 µg/mL of each phenolic compound. These samples differed by the values of conductivity (360 µS and 1380 µS). There was no significant conductivity effect for the recovery of bisphenol A, 2-phenylphenol and nonylphenol. Only for *t*-octylphenol recovery values vary quite significantly. The recovery of this compound was lower for samples with conductivity 360 and 1,380 µS than for the standard sample. The recovery of all tested phenolic compounds from different spiked water samples are presented in Fig. 4.

3.3. Endocrine phenolic compounds from real water samples

To assess the application of selected MIP as sorbent in solid-phase extraction to directly monitor the presence of bisphenol A and alkylphenols in the aquatic environment,

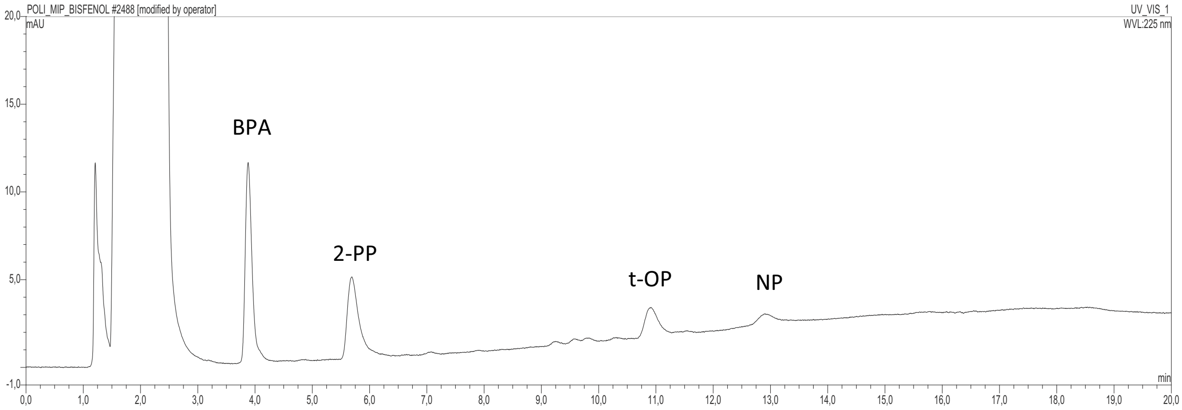


Fig. 2. Typical chromatogram under the optimized solid-phase extraction procedure and separation condition of HPLC for the standard solution of phenolic analytes at the concentration of 0.02 µg/mL in the spiked water sample.

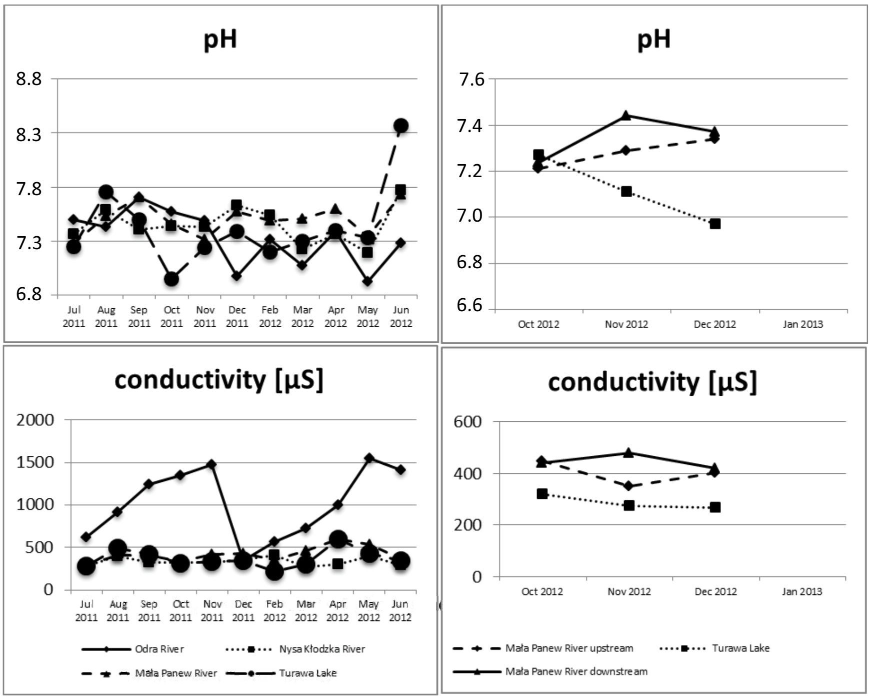


Fig. 3. Changes in pH and conductivity during the year.

Table 2
Analytical characteristics of the MI-SPE-HPLC method

Compound	Calibration equation	r^2	Limit of detection (µg/L)	Limit of quantification (µg/mL)
Bisphenol A	$y = 1.0933x - 0.4635$	0.997	2.5	7.5
2-Phenylphenol	$y = 1.0543x - 0.4968$	0.996	5	15
t-Octylphenol	$y = 0.4831x - 0.2026$	0.998	10	30
Nonylphenol	$y = 0.2949x - 0.0137$	0.994	50	150

surface water samples from the Opole Region were tested. Optimized extraction procedure shows high recovery, good precision and accuracy.

In all samples (obtained from July 2017 to June 2018) detected bisphenol A and 2-phenylphenol above detection limit in the range of concentration 11–415 µg/mL and 20–410 µg/mL, respectively (Table 3). The highest concentration of BPA was observed in samples from Turawa Lake, indicating that the water is polluted with plastic materials for the production of which BPA and their derivatives are

Table 3
Environmental levels of bisphenol A and 2-phenylphenol in surface water's samples ($n = 3$)

Date	Odra River	Nysa Kłodzka River	Mała Panew River	Turawa Lake
Content of bisphenol A (µg/L)				
30th Jul 2017	11 ± 1	102 ± 9	318 ± 34	141 ± 4
27th Aug 2017	81 ± 8	72 ± 7	34 ± 1	72 ± 9
24th Sep 2017	31 ± 4	44 ± 3	37 ± 4	162 ± 19
29th Oct 2017	17 ± 1	12 ± 2	15 ± 2	372 ± 52
27th Nov 2017	31 ± 6	12 ± 1	81 ± 4	158 ± 31
29th Dec 2017	79 ± 7	21 ± 3	60 ± 6	69 ± 9
25th Feb 2018	77 ± 12	38 ± 8	46 ± 6	260 ± 53
31st Mar 2018	51 ± 8	38 ± 5	34 ± 2	225 ± 15
28th Apr 2018	38 ± 9	415 ± 42	53 ± 8	178 ± 32
26th May 2018	66 ± 7	97 ± 14	339 ± 51	46 ± 8
23rd Jun 2018	43 ± 7	40 ± 7	40 ± 4	179 ± 12
Content of 2-phenylphenol (µg/L)				
30th Jul 2017	31 ± 2	41 ± 10	34 ± 5	29 ± 3
27th Aug 2017	47 ± 7	43 ± 7	33 ± 2	105 ± 49
24th Sep 2017	49 ± 4	54 ± 8	50 ± 4	20 ± 1
29th Oct 2017	36 ± 4	38 ± 4	70 ± 19	22 ± 4
27th Nov 2017	64 ± 1	35 ± 8	410 ± 9	93 ± 6
29th Dec 2017	103 ± 12	50 ± 10	86 ± 20	81 ± 15
25th Feb 2018	203 ± 41	103 ± 16	26 ± 1	68 ± 13
31st Mar 2018	192 ± 32	133 ± 21	122 ± 17	131 ± 17
28th Apr 2018	86 ± 15	50 ± 3	65 ± 8	256 ± 19
26th May 2018	61 ± 9	55 ± 6	50 ± 10	98 ± 2
23rd Jun 2018	35 ± 1	30 ± 4	32 ± 2	191 ± 26

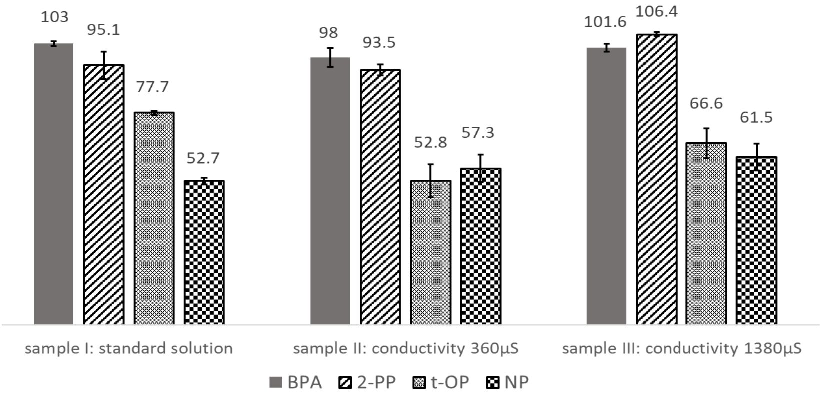


Fig. 4. Recovery of BPA and some APs from spiked water samples of different conductivity.

applied. Moreover, it may result from the more significant accumulation of bisphenol A in stagnant waters than in rivers. The higher concentration of BPA was also observed in few other samples: in Nysa Kłodzka River (April) and Mała Panew River (July, May). There was no correlation between the presence and concentration of BPA in each sample. A significantly higher content of BPA in rivers was expected to find in Odra River than its tributaries. Still, only some waters samples, collected from September 2017 to April 2018, showed this correlation. BPA can easily bind to the river's sediments; therefore, it was not transferred to the main river.

The highest concentration of 2-phenylphenol in rivers was observed in the winter and early spring months, while in the Turawa Lake – from March to June 2012. This substance is widely used in industry for the production of pesticides, rubber chemicals, food packaging, as an intermediate for dyes and food preservatives, and also in the

Table 4
Environmental levels of bisphenol A and 2-phenylphenol in surface water's samples ($n = 3$)

Date	Mała Panew River upstream	Turawa Lake	Mała Panew River downstream
Content of bisphenol A (μg/L)			
13th Oct	97 ± 16	209 ± 23	143 ± 7
10th Nov	124 ± 7	140 ± 6	127 ± 6
16th Dec	276 ± 15	83 ± 19	158 ± 8
6th Jan	245 ± 12	115 ± 6	60 ± 12
Content of 2-phenylphenol (μg/L)			
13th Oct	109 ± 4	112 ± 4	132 ± 5
10th Nov	226 ± 5	274 ± 32	242 ± 20
16th Dec	259 ± 17	156 ± 22	231 ± 41
6th Jan	199 ± 4	132 ± 23	184 ± 32

timber industry. Therefore it may be directly released to the environment through various waste streams, mainly from industrial wastewater.

The environmental levels of BPA and 2-PP in selected water samples are shown in Table 4. None of the tested surface waters did not reveal the presence of both *t*-octylphenol and nonylphenol, despite the use of these substances in industry and agriculture (pesticides).

4. Conclusions

MI-SPE method with HPLC-DAD was the developed and validated for the simultaneous determination of endocrine phenolic compounds from environmental water samples. This SPE procedure for preconcentration of selected analytes and remove of matrix interferents, showed high recovery, good selectivity, precision and accuracy. This method is straightforward, give reliable results and allows the determination of trace amounts of some phenolic compounds in waters samples.

It is believed that a significantly better detection limit of bisphenol A and alkylphenols will be obtained if this molecularly imprinted solid-phase extraction method is coupled with more sensitive detectors (e.g., fluorescence or mass spectrum detector).

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