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Determination of Micropollutants in Water Samples from Swimming Pool Systems

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Abstract: The present study investigated the occurrence of selected micropollutants, including emerging contaminants from a group of pharmaceuticals and personal care products (PPCPs) in water samples from swimming pool systems. The study area was selected based on the lack of available information regarding suspected contamination of swimming pool water by PPCPs. The variety and concentration of chemical compounds in these aquatic systems can be quite diversified, presenting a challenge in terms of both purification and quality control. Determination of PPCPs requires very sensitive analytical methods that make it possible to confirm the presence of tested compounds in a complex organic extract. In this field, gas chromatography-mass spectrometry (GC-MS) can be used. With this system, selected ion monitoring can be performed, which reduces the detection limits of the investigated analyte. This paper aims to present an analytical method and strategy that can be adapted to obtain information on the composition of water in swimming pool systems. The sample preparation methodology, including Solid Phase Extraction, has been developed for the trace determination of two pharmaceuticals—caffeine, carbamazepine—and one sunscreen constituent—benzophenone-3—in swimming pool water samples.

Keywords: GC-MS; Solid Phase Extraction (SPE); micropollutants; swimming pools systems; swimming pool water; pharmaceuticals and personal care products (PPCPs)

1. Introduction

Maintaining the microbial water quality in order to inhibit the spread of infections and diseases is the priority for all swimming pool owners and managers. According to sanitary and hygienic guidelines, disinfection with chlorine compounds is required in public swimming pools [1,2]. There are a number of disinfectants that have been used in swimming pools with the potential to produce a wide range of disinfection by-products (DBPs) through reaction with organic and inorganic matter; this has been well established from studies on disinfection of drinking water. Due to the recirculation technology that is applied, higher chlorination levels, higher organic matter content, and much more DBPs are formed in swimming pool systems compared to drinking water [3].

There are many studies on chemical contaminants in swimming pools focusing on the occurrence of DBPs [3–6]. However, some authors have concluded that further research is needed to evaluate potential health risk not only from DBPs but also from other chemicals occurring in swimming pools [7,8]. Research on pharmaceuticals and personal care products (PPCPs) in swimming pools are still in their infancy and available data are limited.

The most commonly identified compounds from PPCPs group in swimming pools around the world include caffeine, carbamazepine, and benzophenone-3. Caffeine—a stimulant very popular in body lotions, bath lotions, and creams—was found in swimming pools by Weng et al. [9], Suppes et al. [10], and Teo et al. [11]. Ekowati et al. [12] proved carbamazepine to be ubiquitous in swimming pools

(27 from 51 water samples), as it occurred in more than half of all the samples collected and was especially prevalent in outdoor pools (67%) and spas (67%). The growing consumption of pharmaceuticals, including carbamazepine, together with their incomplete removal in wastewater treatment plants implies the occurrence of these compounds in natural water resources [13]. Introduced to the pool, they circulate and may accumulate. Benzophenone-3 is one of the most popular UV-filter, an ingredient found in sunscreens. Fourteen selected UV filters were analyzed from 17 pools in duplicates by Ekowati et al. [12]. Results showed that all the samples contained at least one UV filter (>LOD) and that all 14 UV filters selected were present at least in one sample, mainly benzophenone-3 or its major human metabolites. This compound was also identified in swimming pools by Suppes et al. [10], Lambropoulou et al. [14], Giokas et al. [15], Cuderman and Heath [16], Zwiener et al. [17] and Vidal et al. [18].

PPCPs are designed to be biologically active, including at low concentrations. Long-term exposure to the PPCPs mixture may potentially cause negative health effects. Moreover, their degradation in swimming pool water treatment systems is possible and by-products of PPCPs may be more relevant to the health of swimmers than their parent compound [19]. The fact that swimmers have direct contact with the analyzed compounds and their by-products, means it is necessary to investigate the occurrence of PPCPs in swimming pools.

The determination of PPCPs requires very sensitive analytical methods that enable the confirmation of the presence of tested compounds in a complex organic extract. The variety and concentration of chemical compounds in complex aquatic systems such as swimming pool water is quite diversified, presenting a challenge in terms of quality control. In this field, highly sophisticated equipment, such as gas or liquid chromatography with mass spectrometry (GC-MS or LC-MS) can be used. These detection methods are commonly used as analytical techniques to identify and quantify water contaminants such as PPCPs [20–25]. They enable the detection of PPCPs from different matrices at sub-ng/g levels [26]. There are many disadvantages and advantages of both LC-MS and GC-MS. There is high importance of selecting the appropriate analysis techniques to obtain the best results. The nature and complexity of samples are key factors in choosing the best technique [26]. Pharmaceuticals consist of polar compounds that are soluble in both water and polar solvents, which is a particular advantage of LC-MS analysis. On the other hand, personal care products (PCPs) are relatively non-polar. Furthermore, they are more soluble and better extracted in relatively nonpolar organic solvents [26]. GC-MS is a highly efficient tool that is widely used to analyze PCPs at extremely low levels from environmental samples [26].

Both GC-MS and LC-MS analysis require appropriate sample preparation. The essential preparation step is the extraction. Solid phase extraction (SPE) or liquid-liquid extraction (LLE) are reliable ways to perform this step. LLE has been proven to be an efficient technique; however, it is a reagent consuming procedure and cannot be easily automated. As a result, an alternative method—SPE— has been developed. When compared to other sample preparation processes, SPE offers lower cost due to lower solvent and reagent consumption and greater recoveries as the sample transfer is minimal [27]. Despite the undoubted advantages, SPE does not always perform its task. This is due to the physicochemical properties of some compounds that strongly adsorbed on the surface of the laboratory vessel walls. This adsorption may cause high loss of the analyte. In the liquid extraction method, the solvent is added directly to the sample, which allows the analytes adsorbed on the laboratory vessel walls to be rinsed.

Both liquid and gas chromatography can possess different detection limits, recoveries, accuracy, and repeatability of obtained results. These features depend on the type of analyzed compound and the conditions of sample extraction.

This paper presents a selection of procedure for determining the concentration of three compounds from the macro-group of PPCPs. The goal of this study is to select the type of SPE tube, the extraction process conditions, and the performance parameters of chromatograph during the determinations of the substances.

2. Materials and Methods

The analytical standards of micropollutants—carbamazepine (CBZ), caffeine (CAF), and benzophenone-3 (BP-3)—were supplied by Sigma-Aldrich (Poznań, Poland). The properties of the tested compounds are summarized in Table 1. Organic solvents methanol and acetonitrile of purity grade >99.8% and >99.5% respectively, by Avantor Performance Materials Poland S.A. were also used. Disposable Supelclean™ tubes by Supelco were applied to solid phase extraction. Six types of SPE tubes were tested—ENVI™-8, ENVI™-18, LC™-8, LC™-18, LC™-CN, and LC™-Ph. They are compared in Table 2. The extract was analyzed using a gas chromatograph coupled to mass spectrometry (GC-MS) with Electronic Ionization, Model 7890B by Perlan Technologies (Warszawa, Poland). The extract was separated in SLB™-5 ms Capillary GC Column of Supelco with an internal diameter of 0.25 mm, a length of 30 m, and a layer thickness of 0.25 µm.

In this work, the method of internal standards (IS-mirex) was used to improve the precision of quantitative analysis. The purpose of the internal standard was that it would behave similarly to the analyte but provide a signal that can be distinguished from that of the analyte.

Table 1. Characteristics of tested compounds.

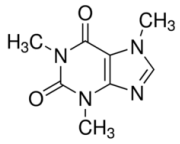
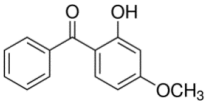
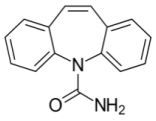
Standard	Structural Formula	Molecular Formula	Molar Mass (g/mol)	CAS Number	Purity
Caffeine (CAF)		$C_8H_{10}N_4O_2$	194.19	58-08-2	>99%
Benzophenone-3 (BP-3)		$C_{14}H_{12}O_3$	228.24	131-57-7	98%
Carbamazepine (CBZ)		$C_{16}H_{12}N_2O$	236.27	298-46-4	>99%

Table 2. Characteristics of Supelclean™ tubes applied to solid phase extraction.

Tube Type	Bed Weight (g)	Tube Volume (mL)	Carbon Loading (%)	Bed Type
ENVI-8	1	6	14	C_8 (octyl)
ENVI-18	1	6	17	C_{18} (octadecyl)
LC-8	0.5	6	7	C_8 (octyl)
LC-18	1	6	11.5	C_{18} (octadecyl)
LC-CN	0.5	6	7	Cyano
LC-Ph	0.5	3	5.5	Phenyl

3. Results and Discussion

The optimum experimental conditions for the extraction and quantification of all selected analytes were investigated by means of an experimental design procedure, the results of which are presented.

3.1. The Linearity of the Mass Detector Response

The following GC-MS (EI) operating parameters have been determined:

- the oven temperature program: 80 °C (6 min), 5 °C/min to 260 °C, 20 °C/min to 300 °C
- the support phase: helium with a flow of 1.1 mL/min
- injector: 250 °C
- injection mode: splitless

- injection speed: 300 µL/min
- ion source: 230 °C
- ion trap: 150 °C
- ion recording mode: 50 ÷ 700 m/s

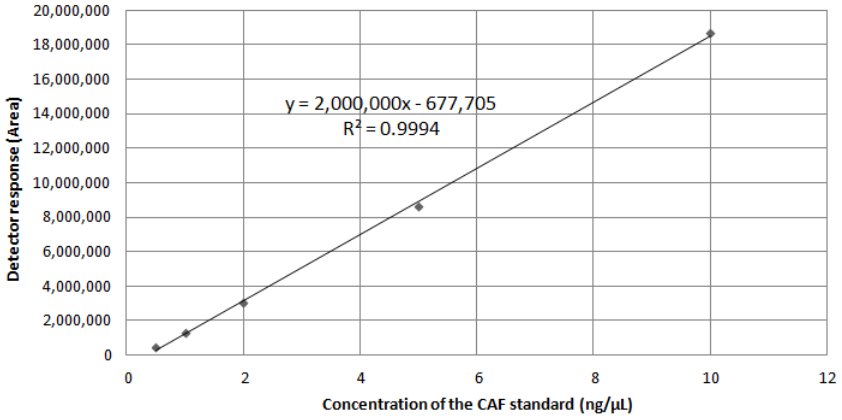
In order to calibrate the mass detector, the calibration curves were prepared based on standard solutions prepared in methanol in a concentration range from 0.5 to 10 ng/µL. The linearity of the mass detector response was examined. It was checked by linear regression (Figure 1). Five repetitions were made to validate these calibration curves. Parameters of calibration curves are presented in Table 3.

Table 3. Parameters of calibration curves for determining micropollutants by gas chromatography-mass spectrometry (GC-MS).

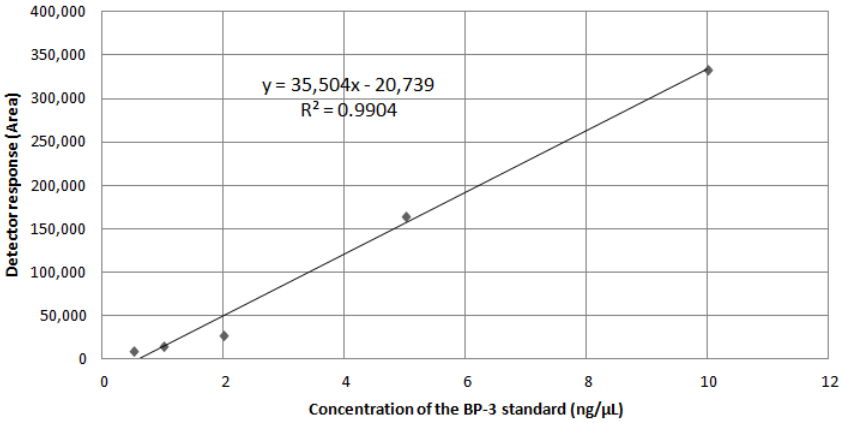
Standard	$t_R \pm SD$	R^2	a	S_a	b	S_b
CAF	19.37 ± 0.01	0.99	2,000,000	316,802	−677,705	459,921
BP-3	22.46 ± 0.02	0.99	35,504	2019	−20,739	2931
CBZ	24.19 ± 0.02	0.95	766,841	295,337	936,453	428,759

Note: t_R—the retention time; SD—the standard deviation; R^2—the correlation coefficient; a—the directional factor; S_a—the standard deviation of directional factor; b—the free term; S_b—the standard deviation of free term.

The obtained values of R^2 coefficient show the linearity of the detector's response. Retention times of compounds allow for proper separation and appropriate identification in complex water matrices. The standard deviations of tR are acceptable.

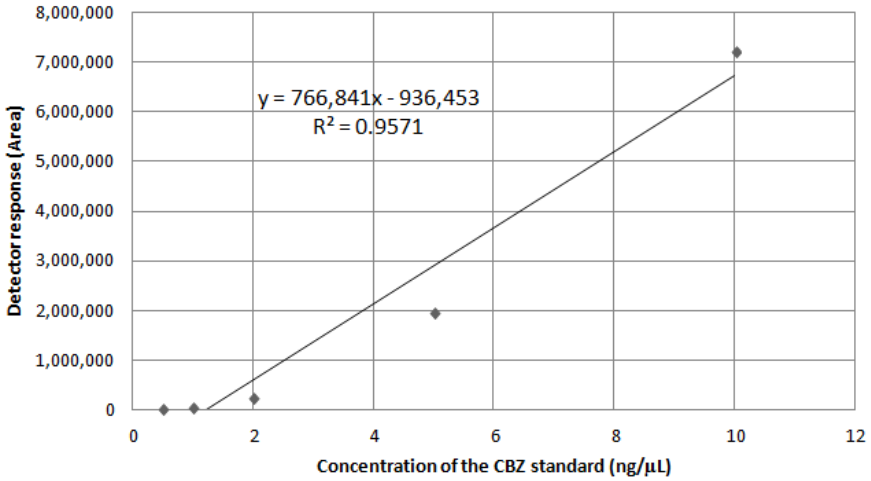


(**a**)



(**b**)

Figure 1. *Cont.*



(**c**)

Figure 1. Calibration curve by GC-MS for (**a**) caffeine (CAF), (**b**) benzophenone-3 (BP-3), and (**c**) carbamazepine (CBZ).

3.2. The Repeatability of the Quantitative Results

In the process of identifying and assessing the concentration of micro-organic compounds in swimming pools, the repeatability of the quantitative results is of key importance. Table 4 shows the values of the coefficient of variation (CV) that is a measure of the repeatability of the measurements. The limit of detection (LOD) was also determined and presented in Table 4. It determines the lowest amount of a substance that can be distinguished from the absence of that substance within a certain confidence interval [18]. The obtained values of CV did not exceed 3%, confirming the high repeatability of the conducted measurements. The analysis of repeatability was also made using peak areas of mass ions (*m*/*z*), which were corrected with areas obtained for the constant content of the internal standard.

Table 4. Coefficient of Variation (CV) for five concentration levels of tested micropollutants.

Standard	CV (%)					LOD (ng/L)
	0.5 ng/µL	1.0 ng/µL	2.0 ng/µL	5.0 ng/µL	10.0 ng/µL	
CAF	0.66	1.39	1.81	1.67	2.25	0.02
BP-3	1.32	1.41	2.28	2.08	0.95	0.02
CBZ	2.81	2.89	2.68	1.59	1.66	0.10

3.3. Sample Preparation Procedure

The main step in developing an analytical procedure for the determination of compounds in pool water is the selection of a sample preparation procedure. Because of the complexity of the matrix and the low concentrations of analytes, it is necessary to isolate the analytes from the samples. In our study, solid phase extraction was used to separate the compounds from swimming pool water according to the following steps:

- conditioning: 10 mL of solvent—methanol or acetonitrile or methanol–acetonitrile mixture (5 mL methanol and 5 mL of acetonitrile), speed 10 mL/min
- washing 5.0 mL of deionized water
- dosing of water samples (volume of 1 L in case of the real swimming pool water extraction or 20 mL in the case of the standard solution extraction)
- drying 5 min under vacuum
- elution: 3 mL of solvent—methanol or acetonitrile or acetonitrile–methanol mixture (1.5 mL of acetonitrile and 1.5 mL of methanol), speed 10 mL/min

The optimization of extraction conditions was performed by searching for the appropriate combination of SPE tube type and solvents used for both conditioning and elution. It was carried out by inserting the standard at the concentration level of 1 mg/L into the deionized water matrix. It was then subjected to an SPE process using different type of tubes and different solvents. Recovery and limit of quantification (LOQ) were examined for each method of sample preparation. They are listed in Table 5. Based on these parameters, the most optimal methodology was chosen. Conditioning with a mixture of methanol and acetonitrile and extraction in the ENVI-18 tube was considered the best suited. The worst results were obtained after the conditioning with a mixture of methanol and acetonitrile and extraction in the LC-CN tube.

Table 5. Recovery and limit of quantification (LOQ) for various combinations of SPE tube types and solvents.

Solvents	SPE Tube Type	Parameter	CAF	BP-3	CBZ
Methanol	ENVI-8	Recovery (%)	88.6	100	100
		LOQ (ng/L)	0.63	2.78	1.51
	ENVI-18	Recovery (%)	100	100	100
		LOQ (ng/L)	0.57	2.07	1.18
	LC-8	Recovery (%)	79.8	83.5	66.2
		LOQ (ng/L)	0.66	2.40	1.77
	LC-18	Recovery (%)	95.4	75.3	100
		LOQ (ng/L)	0.91	4.07	2.08
	LC-CN	Recovery (%)	40.6	100	100
		LOQ (ng/L)	3.23	3.39	1.69
	LC-Ph	Recovery (%)	100	100	72
		LOQ (ng/L)	0.81	2.56	2.03
Acetonitrile	ENVI-8	Recovery (%)	82.7	100	93
		LOQ (ng/L)	0.37	1.82	1.26
	ENVI-18	Recovery (%)	85.1	82.2	100
		LOQ (ng/L)	0.43	2.31	1.18
	LC-8	Recovery (%)	100	100	94.2
		LOQ (ng/L)	1.27	7.19	4.29
	LC-18	Recovery (%)	99.3	78.6	100
		LOQ (ng/L)	1.12	8.06	3.62
	LC-CN	Recovery (%)	27.6	100	82.5
		LOQ (ng/L)	1.14	1.52	1.06
	LC-Ph	Recovery (%)	100	73.7	92.5
		LOQ (ng/L)	0.25	2.04	1.04
Methanol + Acetonitrile	ENVI-8	Recovery (%)	97	100	85
		LOQ (ng/L)	2.40	3.68	3.31
	ENVI-18	Recovery (%)	100	100	100
		LOQ (ng/L)	0.84	0.95	0.87
	LC-8	Recovery (%)	86.2	100	90
		LOQ (ng/L)	0.77	1.10	1.24
	LC-18	Recovery (%)	100	100	100
		LOQ (ng/L)	0.82	2.62	2.51
	LC-CN	Recovery (%)	36.7	85.7	77.7
		LOQ (ng/L)	7.58	9.52	10.64
	LC-Ph	Recovery (%)	100	100	100
		LOQ (ng/L)	2.92	7.35	9.52

Recovery studies to evaluate the percentage of analyte extracted from swimming pool water samples were conducted. Table 6 summarizes results obtained in the most optimal solid phase extraction methodology for the various matrices. It was carried out by inserting the standard at the concentration level of 1 mg/L into the different water matrices—the deionized water, the tap water,

and the swimming pool water. The lowest recovery was obtained for tap water. The recoveries of both deionized water and swimming pool water was 100%. Based on the calculated recovery factors, the accuracy of the results obtained from the chosen analytical method was very good. The repeatability of the results, measured as the standard deviation, was satisfactory; its value was in the range 1 to 10%.

Table 6. Recoveries obtained in the most optimal solid phase extraction methodology (methanol + acetonitrile and ENVI-18 tube) for different matrices.

Matrix	Recovery ± SD (%)		
	CAF	BP-3	CBZ
Deionized water	100 ± 2.4	100 ± 9.9	100 ± 10.0
Tap water	92.5 ± 2.8	95.7 ± 1.2	98.4 ± 8.2
Swimming pool water	100 ± 2.2	100 ± 5.9	100 ± 5.4

The limits of quantification of tested compounds in different matrices are presented in Table 7. The lowest LOQs were obtained for swimming pool water, while the highest were observed for deionized water. The observed differences show the influence of organic and inorganic substances presence in water matrix on the LOQ value.

Table 7. Limits of Quantification obtained in the most optimal solid phase extraction methodology (methanol + acetonitrile and ENVI-18) and the measurements of organic and inorganic substance presence for different matrices.

Matrix				LOQ (ng/L)		
Type	TOC (mg/L)	UV_{245} (-)	Conductivity (mS/cm)	CAF	BP-3	CBZ
Deionized water	0.000	0.000	0.000	0.84	0.95	0.87
Tap water	0.159	0.003	0.178	0.78	0.88	0.83
Swimming pool water	7.062	0.082	2.117	0.69	0.75	0.71

Note: TOC—Total Organic Carbon, UV_{245}—absorbance in 1 mL sample in wavelength 254 nm.

3.4. Analysis of Real Samples

The procedure developed in the presented study was applied to several samples obtained from swimming pools located in the region of Silesia, Poland. The quantification of the samples was carried out according to the procedure described previously, and the concentrations of detected analytes were obtained from an average value of three measurements. The results obtained (Table 8) indicated that the presented procedure could be successfully applied to PPCPs residue determination in real water samples. However, it was observed that sampling strategy is a critical parameter for the representative monitoring of these compounds. The concentration levels of trace contaminants in swimming pool water vary a lot depending on many factors, for example, point and time of sampling (Figure 2), type of swimming pool basin, and the number of swimmers [28,29]. They also vary due to the water recirculation applied [30].

Table 8. Pharmaceuticals and personal care products (PPCPs) found in swimming pools collected throughout the Silesia region in Poland and the measurements of organic and inorganic substance presence.

Sample	TOC [mg/L]	UV_{245} (-)	Conductivity (mS/cm)	Concentration (ng/L)					
				CAF	SD_{CAF}	BP-3	SD_{BP-3}	CBZ	SD_{CBZ}
SP1	16.98	0.046	2.030	1.03–1.09	0.05	5.59–10.84	2.25	4.71–7.17	0.82
SP2	7.63	0.051	0.717	10.50–13.64	1.77	34.55–175.84	70.97	42.20–51.44	5.01
SP2	12.25	0.099	1.267	<LOQ	-	1.86–4.12	0.82	3.67–3.70	0.02
SP4	12.12	0.077	0.964	1.02–1.40	0.23	49.27–52.29	2.13	9.43–9.93	0.36
SP5	1.04	0.003	0.689	1.45–1.54	0.06	2.10–3.21	0.69	7.02–8.86	2.58

Note: TOC—Total Organic Carbon, UV_{245}—-absorbance in 1 mL sample in wavelength 254 nm, SD—Standard Deviation.

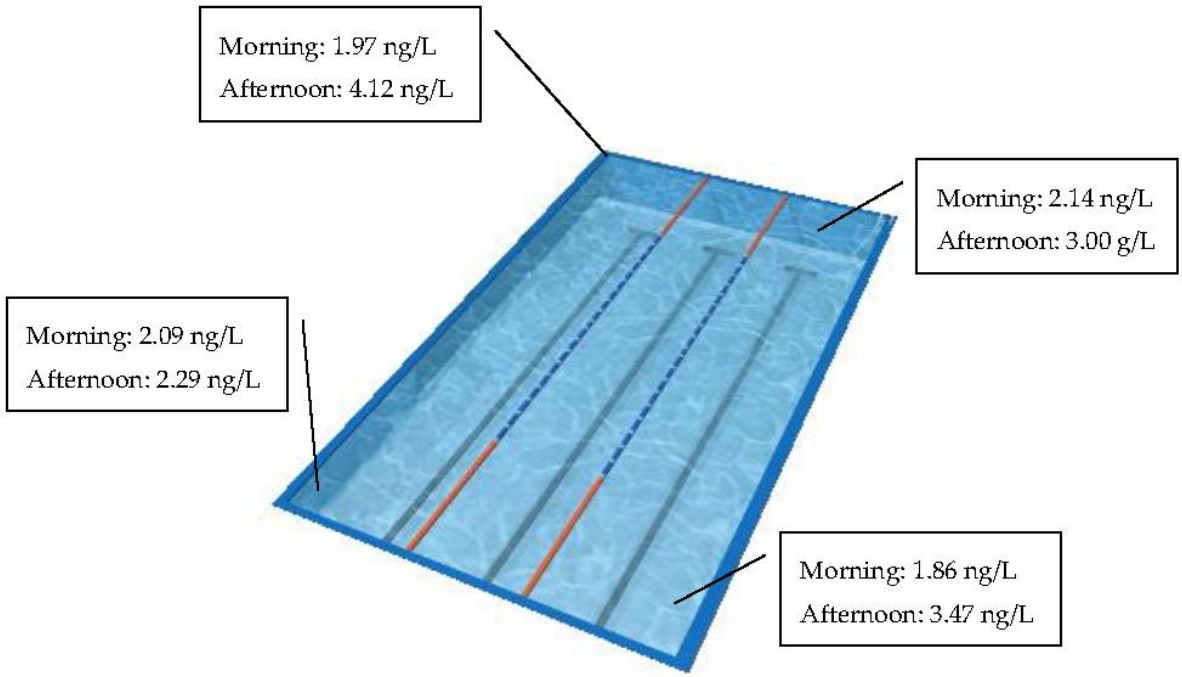


Figure 2. BP-3 concentrations depending on the point and time of sampling.

4. Conclusions

An analytical methodology for the trace determination of three widely used PPCPs in swimming pool water is presented. The developed methodology can be used for analytical control of swimming pool water treatment processes from selected pharmaceuticals and personal care products. It was proven that the presented analytical procedure enables the quantification of caffeine, carbamazepine, and benzophenone-3 with satisfactory repeatability and accuracy. The selected compounds could be efficiently determined under the optimized experimental conditions. The obtained recovery values ensure the possibility of full quantitative control of the tested micropollutants in samples collected from swimming pool water systems.

The different physicochemical composition of water affects LOQ. The values of LOQ obtained for swimming pool water were lower compared to deionized and tap water.

The developed methodology was successfully applied for monitoring PPCP compounds in swimming pool water samples at the ng/L levels. Considering the European Union directive for bathing and swimming pool waters, this paper presents an analytical tool for the incorporation of PPCP residuals in bathing water quality criteria.

As sampling strategy is a critical parameter for the representative monitoring of micropollutants, it is necessary to determine the point where the worst results occur. Accumulation of micropollutants in some point may also affect other basic water quality parameters that are constantly monitored. It is important that pool water quality control is carried out in a critical location.

Author Contributions: A.L. and E.K. conceived and designed the experiments, performed the experiments, and analyzed the data under the supervision of M.D.; M.D. contributed reagents, materials, and analysis tools; A.L. wrote the paper under the supervision and review of M.D. and E.K.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. WHO. Guidelines for Safe Recreational Water Environments. Volume 2: Swimming Pools and Similar Environments. 2006. Available online: www.who.int/water_sanitation_health/water-quality/recreational/en/ (accessed on 25 September 2017).
2. DIN 19643 1-4:2012-11. *Aufbereitung von Schwimm und Badebeckenwasser (Treatment of Water of Swimming Pools and Bathss)*; Beuth: Berlin, Germany, 2012.
3. Chowdhury, S.; Alhooshani, K.; Karanfil, T. Disinfection by-products in swimming pool: Occurrences, implications and future needs. *Water Res.* **2014**, *53*, 68–109. [CrossRef] [PubMed]
4. Kanan, A.; Karanfil, T. Formation of disinfection by-products in indoor swimming pool water: The contribution from filling water natural organic matter and swimmer body fluids. *Water Res.* **2011**, *45*, 926–932. [CrossRef] [PubMed]
5. Lee, J.; Jun, M.J.; Lee, M.H.; Eom, S.W.; Zoh, K.D. Production of various disinfection byproducts in indoor swimming pool waters treated with different disinfection methods. *Int. J. Hyg. Environ. Health* **2010**, *213*, 465–474. [CrossRef] [PubMed]
6. Wyczarska-Kokot, J. Comparison of chloramine concentration in swimming pool water depending on swimming pool intended use. *Ecol. Chem. Eng. A* **2015**, *22*, 27–37. [CrossRef]
7. Terasaki, M.; Makino, M. Determination of chlorinated by-products of parabens in swimming pool water. *Int. J. Environ. Anal. Chem.* **2008**, *88*, 911–922. [CrossRef]
8. Teo, T.L.L.; Coleman, H.M.; Khan, S.J. Chemical contaminants in swimming pools: Occurrence, implications and control. *Environ. Int.* **2015**, *76*, 16–31. [CrossRef] [PubMed]
9. Weng, S.C.; Sun, P.; Ben, W.W.; Huang, C.H.; Lee, L.T.; Blatchley, E.R. The presence of pharmaceuticals and personal care products (PPCPs) in swimming pools. *Environ. Sci. Technol. Lett.* **2014**, *1*, 495–498. [CrossRef]
10. Suppes, L.M.; Huang, C.H.; Lee, W.N.; Brockman, K.J. Sources of pharmaceuticals and personal care products in swimming pools. *J. Water Health* **2017**, *15*, 829–833. [CrossRef] [PubMed]
11. Teo, T.L.L.; Coleman, H.M.; Khan, S.J. Occurrence and daily variability of pharmaceuticals and personal care products in swimming pools. *Environ. Sci. Pollut. Res.* **2016**, *23*, 6972–6981. [CrossRef] [PubMed]
12. Ekowati, Y.; Buttiglieri, G.; Ferrero, G.; Valle-Sistac, J.; Diaz-Cruz, M.S.; Barceló, D.; Petrovic, M.; Villagrasa, M.; Kennedy, M.D.; Rodríguez-Roda, I. Occurrence of pharmaceuticals and UV filters in swimming pools and spas. *Environ. Sci. Pollut. Res. Int.* **2016**, *23*, 14431–14441. [CrossRef] [PubMed]
13. Martínez-Hernández, V.; Meffe, R.; Kohfahl, C.; de Bustamante, I. Investigating natural attenuation of pharmaceuticals through unsaturated column tests. *Chemosphere* **2017**, *17*, 292–302. [CrossRef] [PubMed]
14. Lambropoulou, D.A.; Giokas, D.L.; Sakkas, V.A.; Albanis, T.A.; Karayannis, M.I. Gas chromatographic determination of 2-hydroxy-4-methoxybenzophenone and octyldimethyl-p-aminobenzoic acid sunscreen agents in swimming pool and bathing waters by solidphase microextraction. *J. Chromatogr. A* **2002**, *967*, 243–253. [CrossRef]
15. Giokas, D.L.; Sakkas, V.A.; Albanis, T.A. Determination of residues of UV filters in natural waters by solid-phase extraction coupled to liquid chromatography-photodiode array detection and gas chromatography-mass spectrometry. *J. Chromatogr. A* **2004**, *1026*, 289–293. [CrossRef] [PubMed]
16. Cuderman, P.; Heath, E. Determination of UV filters and antimicrobial agents in environmental water samples. *Anal. Bioanal. Chem.* **2007**, *387*, 1343–1350. [CrossRef] [PubMed]
17. Zwiener, C.; Richardson, S.D.; De Marini, D.M.; Grummt, T.; Glauner, T.; Frimmel, F.H. Drowning in disinfection byproducts? Assessing swimming pool water. *Environ. Sci. Technol.* **2007**, *41*, 363–372. [CrossRef] [PubMed]
18. Vidal, L.; Chisvert, A.; Canals, A.; Salvador, A. Ionic liquid-based single-drop microextraction followed by liquid chromatography-chromatographyultraviolet spectrophotometry detection to determine typical UV filters in surface water samples. *Talanta* **2010**, *81*, 549–555. [CrossRef] [PubMed]
19. Bottoni, P.; Bonadonna, L.; Chirico, M.; Caroli, S.; Záray, G. Emerging issues on degradation by-products deriving from personal care products and pharmaceuticals during disinfection processes of water used in swimming pools. *Microchem. J.* **2014**, *112*, 13–16. [CrossRef]
20. Koutsouba, V.; Heberer, T.; Fuhrmann, B.; Schmidt-Baumler, K.; Tsipi, D.; Hiskia, A. Determination of polar pharmaceuticals in sewage water of Greece by gas chromatography-mass spectrometry. *Chemosphere* **2003**, *51*, 69–75. [CrossRef]

21. Benotti, M.J.; Trenholm, R.A.; Vanderford, B.J.; Holady, J.C.; Stanford, B.D.; Snyder, S.A. Pharmaceuticals and endocrine disrupting compounds in U.S. drinking water. *Environ. Sci. Technol.* **2009**, *43*, 597–603. [CrossRef] [PubMed]
22. Kim, S.D.; Cho, J.; Kim, I.S.; Vanderford, B.J.; Snyder, S.A. Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking, and waste waters. *Water Res.* **2007**, *41*, 1013–1021. [CrossRef] [PubMed]
23. Vanderford, B.J.; Pearson, R.A.; Rexing, D.J.; Snyder, S.A. Analysis of endocrine disruptors, pharmaceuticals, and personal care products in water using liquid chromatography/tandem mass spectrometry. *Anal. Chem.* **2003**, *75*, 6265–6274. [CrossRef] [PubMed]
24. Ollers, S.; Singer, H.P.; Fässler, P.; Müller, S.R. Simultaneous quantification of neutral and acidic pharmaceuticals and pesticides at the low-ng/l level in surface and waste water. *J. Chromatogr. A* **2001**, *911*, 225–234. [CrossRef]
25. Lee, H.B.; Peart, T.E.; Svoboda, M.L. Determination of endocrine-disrupting phenols, acidic pharmaceuticals, and personal-care products in sewage by solid-phase extraction and gas chromatography-mass spectrometry. *J. Chromatogr. A* **2005**, *1094*, 122–129. [CrossRef] [PubMed]
26. Hao, C.; Zhao, X.; Yang, P. GC-MS and HPLC-MS analysis of bioactive pharmaceuticals and personal care products in environmental matrices. *Trends Anal. Chem.* **2007**, *26*, 569–580. [CrossRef]
27. Rezaee, M.; Assadia, Y.; Milani Hosseini, M.R.; Aghaeea, A.; Ahmadia, F.; Berijania, S. Determination of organic compounds in water using dispersive liquid-liquid microextraction. *J. Chromatogr. A* **2006**, *1116*, 1–9. [CrossRef] [PubMed]
28. MacDougall, D.; Crummett, W.B. Guidelines for Data Acquisition and Data Quality Evaluation in Environmental Chemistry. *Anal. Chem.* **1980**, *52*, 2242–2249. [CrossRef]
29. Lempart, A.; Kudlek, E.; Lempart, M.; Dudziak, M. The presence of compounds from the personal care products group in swimming pool water. *J. Ecol. Eng.* **2018**, *19*, 29–37. [CrossRef]
30. Lempart, A.; Kudlek, E.; Dudziak, M.; Szyguła, A. The impact of the circulation system on the concentration level of micropollutants in the swimming pool water treatment system (in Polish: Ocena wpływu systemu cyrkulacji na poziom stężeń mikrozanieczyszczeń w układzie oczyszczania wody basenowej). *Inżynieria Ekologiczna* **2018**, *1*, 23–31. [CrossRef]