Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.22552

117 (2018) 353–361
June

Concentration levels of selected pharmaceuticals in swimming pool water

Anna Lempart*, Edyta Kudlek, Mariusz Dudziak

Faculty of Energy and Environmental Engineering, of Water and Wastewater Engineering, Silesian University of Technology, Konarskiego 18, 44-100 Gliwice, Poland, emails: anna.lempart@polsl.pl (A. Lempart), edyta.kudlek@polsl.pl (E. Kudlek), mariusz.dudziak@polsl.pl (M. Dudziak)

Received 14 December 2017; Accepted 27 May 2018

ABSTRACT

This paper presents the concentration levels of three selected pharmaceuticals (carbamazepine, caffeine, benzocaine) in swimming pool water. The research was conducted for four different types of pool basins (sports pool, paddling pool, jacuzzi and water slide). The extraction of micropollutants from the environmental matrix was carried out by solid-phase extraction. The extracts were analyzed using a gas chromatograph coupled to the mass detector. The most commonly identified compound was carbamazepine. Its concentrations ranged 12.27–13.82 ng/L. The least frequently identified pharmaceutical was benzocaine. The research has documented the impact of swimming pool function on the concentration levels of particular micropollutants. The highest concentrations of caffeine were observed in the water slide. Its maximum value was 16.40 ng/L there, while in other basins the highest measured concentration was 5.95 ng/L. The levels of selected pharmaceuticals at various points in the sports basin were also compared. Depending on the point of sampling in the sports basin, the measured concentrations were different. These differences result from the specificity of the swimming pools' hydraulic system: the occurrence of both "dead zones" and zones of good water mixing.

Keywords: Pharmaceuticals; Swimming pool water; Micropollutants

1. Introduction

Constant increase in drug consumption, the incomplete digestibility of therapeutic substances by the consumer and the inability to completely eliminate them in conventional treatment methods results in increased presence of pharmaceutical compounds in the environment. Published literature aimed at determining the environmental concentrations of pharmaceuticals have shown the presence of this type of micropollutants on level of several nanogram per liter to several microgram per liter [1–4]. However, the health effects do not depend only on the concentration of compounds but also on a number of other factors, including: lipophilicity, stability of the compound, potential of bioaccumulation, exposure time, transformation and degradation of the substance. Furthermore, they are designed to be biologically active also at low concentrations [5]. Thus their presence in water, even at very low concentrations, has raised concerns regarding the potential risks to human health. Aquatic environment is persistently fed with anthropogenic sources of chemical compounds of different types, which can affect living organisms in various ways. Their influence on the body's systems may cause changes in their activity [5]. Studies on the occurrence of pharmaceuticals are a challenge in assessing potential human health risks from their exposure to trace concentrations.

The occurrence of pharmaceuticals in swimming pool water showed in recent researches [6–9] is particularly concerning as the swimmer body is indirectly exposed to water containing chemical substances. They may be ingested, inhaled or absorbed by swimmers. For example, it has been estimated that the mean volume of water swallowed by non-adults is 37 mL during 45 min of swimming [10]. Pharmaceutical compounds detected in swimming pool waters all over the world are summarized in Table 1. They are commonly found in the

* Corresponding author.

Presented at the 13th Conference on Microcontaminants in Human Environment, 4–6 December, Czestochowa, Poland, 2017.

environment as well. It is caused by difficulties in the removal of these compounds during conventional drinking water and wastewater treatment [11,12]. In swimming pools, due to the recirculation technology that is applied, they can be present at higher concentration than in the environment. Accumulation of pharmaceuticals in swimming pool water can happen as they are the ingredients of products applied externally and may be washed off the human body during swimming. Moreover, some pharmaceuticals are not completely metabolized by humans and are excreted through urine, while in the typical Olympic pool, up to 230 L of urine can occur. One average swimmer leaves about 70 mL of urine in the pool [13]. Some of them are also resistant to biodegradation thus, may lead to their storage and persistence in the swimming pool water environment [14].

The variety and concentration of chemical compounds in such complex aquatic system as swimming pool water is quite diversified. Different types of substances coexisting in pool water may dangerously interact with one another [15]. Long-term exposure of mixture pharmaceuticals and other chemical compounds may potentially cause negative health effects. Chemical compounds in swimming pools originate from a number of sources, mainly from the source water, from deliberate addition of chemicals or from bathers themselves. They contain organic and inorganic constituents that could act as disinfection by-product (DBP) precursors [8]. Pharmaceuticals have been proven to act as DBP precursors [16–18]. Some of them can be transformed into new products by chlorination [19], some may also suffer degradation due to exposure to sunlight [20]. It was suggested that certain transformation products of pharmaceuticals are more toxic than their parent compound [21]. In addition, pharmaceuticals have been shown to be toxic to living organisms. It has been confirmed in numerous studies using ecotoxicity, genotoxicity, cytotoxicity and phytotoxicity assays [21,22]. Investigations on the potential negative effects of pharmaceutical substances were performed in laboratory samples of model waters with the addition of selected micropollutants [23]. However, it does not show the actual effect of drugs present in the waters as mixtures of all therapeutic groups.

Researches on pharmaceuticals in swimming pools are still in their infancy and available data are limited. Studies on this topic are needed in order to identify the effects of introduction of these chemicals into pools. Furthermore, a wider range of chemicals than far described may occur in swimming pools. They need to be identified in order to enable the determination of the potential risk of exposure of pharmaceuticals and their by-products to swimmers.

Table 1
Pharmaceuticals detected in swimming pool water

Drug class	Pharmaceutical compound	Content	Country	References
Stimulant	Caffeine	30–500 ng/L	United States (Georgia and Indiana)	Weng et al. [6]
Stimulant; anti-inflammatory	Caffeine; ibuprofen	20–1,540 ng/L; 16–83 ng/L	Australia (Sydney)	Teo et al. [7]
β-Blocker	Atenolol	0.6 ng/L	Spain	Ekowati et al. [8]
Antiepileptic	Carbamazepine	1.4 ng/L		
Thiazide diuretics	Hydrochlorothiazide	904 ng/L		
Antibiotics	Metronidazole	3.3 ng/L		
Antibiotics	Ofloxacin	2.1 ng/L		
Antibiotics	Sulfamethoxazole	6.4 ng/L		
Analgesic	Acetaminophen	61.2 ng/L		
Anti-inflammatory	Ibuprofen	171.3 ng/L		
Anti-inflammatory	Ketoprofen	360 ng/L		
Anti-inflammatory	Phenazone	0.8 ng/L		
Anti-inflammatory	Acetaminophen	Not tested[a]	United States (Wisconsin and Minnesota)	Suppes et al. [9]
Statins	Atorvastatin			
Stimulant	Caffeine			
Antiepileptic	Carbamazepine			
Nicotine metabolite	Cotinine			
Anti-inflammatory	Diclofenac			
Antidepressant	Fluoxetine			
Lipid regulator	Gemfibrozil			
Anti-inflammatory	Ibuprofen			
β-Blocker	Metoprolol			
Antidepressant	Paroxetine			
Antibiotic	Sulfamethoxazole			
Antibiotic	Trimethoprim			

[a]Only the frequency of presence was analyzed.

The research presented in this article aimed to determine the concentration levels of pharmaceuticals in four different types of swimming pools. In addition, the concentration distribution at various points of one swimming pool was analyzed. Three compounds that most frequently occurred in the preliminary study [24,25] were selected for this research. They are as follows:

- carbamazepine (CBZ) – psychotropic medicine from the group of anticonvulsants,
- benzocaine (BZC) – an example of local anesthetic,
- caffeine – most often and most widely consumed stimulant.

The toxicity of psychotropic drugs, including carbamazepine, was confirmed by studies on its effect on fish and shellfish [26–28]. The adverse effects of this drug on the development of *Corbicula fluminea* exposed to concentrations ranging from 0.5 to 50 μg/L were observed [29]. Furthermore carbamazepine occurrence may indirectly cause damage to proteins, lipids and DNA structure of cells [30]. Its presence also results in impairment of the fish sperm antioxidant system [31].

Benzocaine is the active ingredient in many pain relievers used externally in the form of ointments, powders or gels, as well as internally as an ingredient in tablets or aerosols to relieve sore throat. Benzocaine is non-toxic, when applied as recommended [32]. However, there have been reports of serious, life-threatening adverse effects with over-application of its both topical or oral products. It has been found to be a cause of seizures, coma, irregular heartbeat, respiratory depression. The oral overdosage can increase the risk of pulmonary aspiration, while excessive use of spray products applied to the mouth or mucous membranes may cause methemoglobinemia [33,34]. Benzocaine may also cause allergic reactions: skin redness and itchiness or anaphylaxis [35].

Caffeine is seen as a relatively harmless substance but over time it reaches a very high concentration in surface waters. It has been widely detected in various aquatic systems. Its removal from sewage is not tested, resulting in a steady increase in caffeine concentrations in the environment. It is also considered to be an indicator of human contamination as it has been proved that the presence of caffeine in waters is closely related to anthropogenic impurities [36,37].

2. Materials and methods

The qualitative and quantitative analysis of organic micropollutants in environmental samples is a multi-stage and time-consuming process. This requires suitable analytical instruments that make it possible to confirm the presence of the tested compounds in a complex organic extract. The reliability of the obtained results depends on the accuracy of the individual sample preparation steps and the precision of the measuring equipment. In this matter, gas chromatography can be used. This technique allows the selected ion monitoring to be performed. It enables the reduction of analyte detection limits.

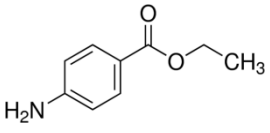
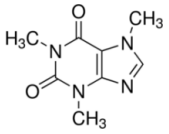
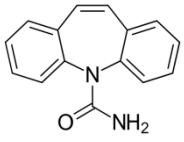
2.1. Materials and reagents

The standards of carbamazepine (CBZ), benzocaine (BZC) and caffeine (CAF) of purity grade >98% were supplied by Sigma-Aldrich (Poznań, Poland) (Table 2). Organic solvents such as methanol and acetonitrile of purity grade >99.8% and >99.5%, respectively, supplied by Avantor Performance Materials Poland S.A. (Gliwice, Poland) were also used. Disposable Supelclean™ ENVI™-18 Tubes packed with octadecyl bed of 1.0 g by Supelco were applied to solid-phase extraction (Table 3).

Table 3
Characteristics of Supelclean™ ENVI™-18 tubes applied to solid-phase extraction

Bed weight (g)	1
Tube volume (mL)	6
Bed capacity (mg)	25–100
Matrix	Silica gel base material
Matrix active group	C18 (octadecyl) bonding
Particle size (μm)	45
Pore volume (mL/g)	0.8
Pore size (Å)	60

Table 2
Characteristics of investigated pharmaceuticals

Pharmaceutical compound	Benzocaine (BZC)	Caffeine (CAF)	Carbamazepine (CBZ)
Synonyms/trade name	Anbesol, Cepacol, Lanacane, Orajel, Anesthesin	1,3,7-Trimethylxanthine, methyltheobromine, guaranine, theine	Tegretol
Structural formula			
Molecular formula	$C_9H_{11}NO_2$	$C_8H_{10}N_4O_2$	$C_{16}H_{12}N_2O$
Molecular weight (g/mol)	165.2	194.2	236.3
CAS number	94-09-7	58-08-2	298-46-4
logP	1.86	–0.07	2.45
pKa (at 25°C)	2.51	14.0	13.9
Water solubility at 25°C (mg/L)	1,310	21,600	17.7

2.2. Analytical procedure

The isolation of micropollutants from the water matrix was carried out by solid-phase extraction in tubes filled with non-polar adsorbent C18. In order to activate the bonded phases and to ensure consistent interaction between the analyte and the sorbent functional groups, the bed was first conditioned in sequence with 5 mL of methanol and 5 mL of acetonitrile. Then it was washed with 5 mL of deionized water. Afterwards 100 mL of water sample was applied. To ensure optimal retention, extraction was carried at a consistent and reduced flow rate of ~1–2 drops/s. After extraction the bed was dried for 5 min under vacuum. The extract was eluted, respectively, with 1.5 mL of acetonitrile and 1.5 mL of methanol.

The extracts were analyzed using a gas chromatograph coupled to mass spectrometry (GC/MS) with electronic ionization, model 7890B by Perlan Technologies (Warszawa, Poland). It combines two techniques to provide the identification of compounds with low detection limits. The extract was separated in a 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. The oven temperature program was as follows: 80°C (6 min), 5°C/min to 260°C, 20°C/min to 300°C. The support phase was helium with a flow of 1.1 mL/min. Sample injections of 1 μL were performed automatically. The mass detector worked in the ion recording mode in the range of 50–700 m/s.

Each sample was analyzed three times. The obtained concentrations of the pharmaceutical compounds are the arithmetical mean of the results obtained by chromatography.

The limits of quantification (LOQ) of the tested pharmaceuticals were, respectively, 0.75 ng/L for BZC, 0.71 ng/L for CBZ and 0.69 ng/L for CAF.

2.3. Water samples

Swimming pool water samples were collected from four different types of indoor pool basins: sports pool, paddling pool, jacuzzi and water slide. Water sampling points were located 30 cm below the pool water surface, in accordance with Standard DIN 19643 [38]. Samples were collected at fixed intervals from various points of basins. Samples of filling waters from taps on each location were also collected. Water samples were collected early in the morning, when the number of swimmers was minimal, in order to minimize the impact of their presence in water on the research results.

Investigated swimming pools are located in Upper Silesia in Poland. Samples were collected in June 2017. According to periodic water quality tests conducted in accredited laboratory (Table 4), the water in all tested pools meets the requirements of Polish law [39]. The results of these analyses were shared by the pool manager. In Table 4, physical and chemical parameters of the water samples collected during the research are also presented. Redox, conductivity and pH were gauged with a multifunctional CX-461 meter (ELMETRON, Zabrze, Poland). The absorbance UV_{254} measured at a universal wavelength of 254 nm of using a Cecil CE1021 spectrophotometer corresponds to the total concentration of organic compounds. It enables the identification of the dissolved organic carbon fraction characterized by a high content of aromatic components, and thus a large potential for DBP formation.

Samples were collected once a day from each of the examined days. Bottles of 1 L volume made of chemically and biologically inert borosilicate glass and equipped with silicon septas were used for the collection, transport and storage of collected water samples. It was important to protect the tested water against light in order to minimize any possible changes in its composition. Samples were immediately transported in a portable refrigerator at a temperature of +4°C to the laboratory in the New Technologies Center of the Institute of Water and Wastewater Engineering of the Silesian University of Technology in Gliwice, where the tests were carried out at once. Each sample was analyzed three times. The obtained concentrations of the pharmaceutical compounds are the arithmetical mean of the results obtained by chromatography. The assignment error was estimated on the basis of standard deviation.

2.4. Characteristics of investigated swimming pools

Sports pool basin, with dimensions of 25 × 12.5 m and variable depth from 1.1 to 1.8 m, is made of stainless steel. This pool in the morning is mainly used for swimming lessons for school-age children (7–12 years). In the evenings there are aqua aerobics classes for the elderly and training sessions for advanced swimmers aged 16–20 years. The average sports pool load is 360 people/d. Paddling pool with a depth of 0.35 m and water temperature of 35°C–36°C is intended mainly for children under 3 years of age. The average paddling pool load is 30 children/d. Jacuzzi allows to take a bath of six people at the same time at a temperature of 36°C. It is very crowded, mainly in the evenings and early in the morning. The main users of this pool are the elderly. The average jacuzzi load is 180 people/d. On average, one person spends 15 min in the jacuzzi. Water slide is very popular mainly by children and young people. The presence of a single person is limited to a few minutes, for the period of slide and slowing down in the special pool. The average load is 600 slides/d. It should be noted that some children slide several times, so this value is probably a bit overestimated.

The water treatment technology is similar in all of investigated swimming pool installations. It bases on the filtration systems equipped with pressure filters filled with multi-layered beds of sand and anthracite. Aluminum hydroxide chloride coagulant is dosed to improve filtration efficiency. Deactivation of all pathogenic organisms is provided by disinfection system. It works in two stages. First, the water is exposed to UV light through a low-pressure lamp. As a second step, automatic dosing of sodium hypochlorite is used.

3. Results and discussion

Both the influence of the swimming pool function on the concentration levels of selected pharmaceuticals (Fig. 1) and the distribution of these concentrations depending on the location of the sampling points (Figs. 2–4) were evaluated.

The most commonly identified compound was carbamazepine. It was present in all tested samples from all type of basins in the concentration range from 12.27 to 13.82 ng/L. The mean values of its measured concentrations were

Table 4
Physical and chemical parameters of the examined water samples and results of periodic water quality tests conducted in accredited laboratory jars

Type of pool	Day	Parameters of water samples				Results from accredited laboratory			
		pH	Absorbance UV_{254} (cm^{-1})	Redox (mV)	Conductivity (mS/cm)	pH	Free chlorine (mg/L)	Combined chlorine (mg/L)	Redox (mV)
Sports Pool						7.30	0.50	0.26	942
	1	7.22	0.035	746	1.1049				
	2	7.45	0.27	734	1.1263				
	3	7.36	0.038	730	0.9822				
	4	7.30	0.022	803	0.9760				
	5	7.33	0.040	770	0.9800				
						7.40	0.47	0.28	890
Paddling						7.30	0.53	0.22	705
pool	1	7.31	0.030	768	0.3985				
	2	7.29	0.010	744	0.3964				
	3	6.98	0.043	740	0.3908				
	4	7.20	0.014	801	0.4340				
	5	7.20	0.038	863	0.5670				
						7.30	0.46	0.30	680
Jacuzzi						7.30	0.63	0.17	932
	1	6.83	0.013	793	1.2208				
	2	7.36	0.0021	770	1.0935				
	3	6.88	0.034	804	1.0049				
	4	6.69	0.000	777	0.9700				
	5	7.12	0.043	863	0.9020				
						7.20	0.89	0.13	902
Water slide	1	Not tested[a]							
	2	7.57	0.027	680	1.1537				
	3	7.24	0.040	782	0.9620				
	4	7.44	0.017	718	0.9700				
	5	7.44	0.037	790	0.9360				

[a]Water slide was closed and excluded from use in the first day of research.

13.16 ng/L in sport basin, 12.51 ng/L in Jacuzzi, 12.69 ng/L in paddling pool and 13.19 ng/L in water slide. Both in paddling pool, jacuzzi, sports pool and water slide, the average concentration of carbamazepine was the highest from all pharmaceuticals selected to this research. In the study conducted by Ekowati et al. [8], carbamazepine was also found to be ubiquitous; however, its concentration levels were much lower (up to 1.4 ng/L) [8]. The frequent occurrence of carbamazepine at relatively high concentrations may suggest that this compound is not removed in conventional systems used for swimming pool water treatment.

The highest concentrations of caffeine were observed in the water slide. Its mean value was 12.81 ng/L there, while in other basins the highest measured concentration was 5.95 ng/L. The average caffeine concentration in sports pool was 3.68 ng/L, in jacuzzi 2.15 ng/L and in paddling pool 1.75 ng/L. It did not occur in every collected samples. The caffeine concentrations detected in this study are not comparable with those that were reported by Weng et al. [6] and Teo et al. [7]. Possible reason for the lower levels could be the low usage of the pools at the time of sampling. The samples were collected early in the morning, while the biggest load of users exists in the evenings. Teo et al. [7] observed that the levels of caffeine are lower at the start of each day and increase throughout the day with the highest concentration occurring during the last sampling of the day. It was previously proposed to use the caffeine as possible water monitoring indicator for organic contamination in environmental waters [40]. Further detailed studies that will investigate the relationship between caffeine concentrations and the amount of anthropogenic contamination may let the same or similar idea to be applied in swimming pools.

The least frequently identified pharmaceutical compound was benzocaine. It was present once in paddling pool (3.55 ng/L) and once in water slide (3.51 ng/L). In jacuzzi it was observed two times, in the first and in the last day of the research in similar concentrations: 3.67 and 3.68 ng/L. So far the presence of benzocaine in swimming pool water has not been reported in any literature. As it is a component of many pain relievers applied externally, its occurrence support the importance of showering before entering a swimming pool.

The maps of daily concentrations changes in various points of sports pool are shown in Figs. 2–4. In paddling pool,

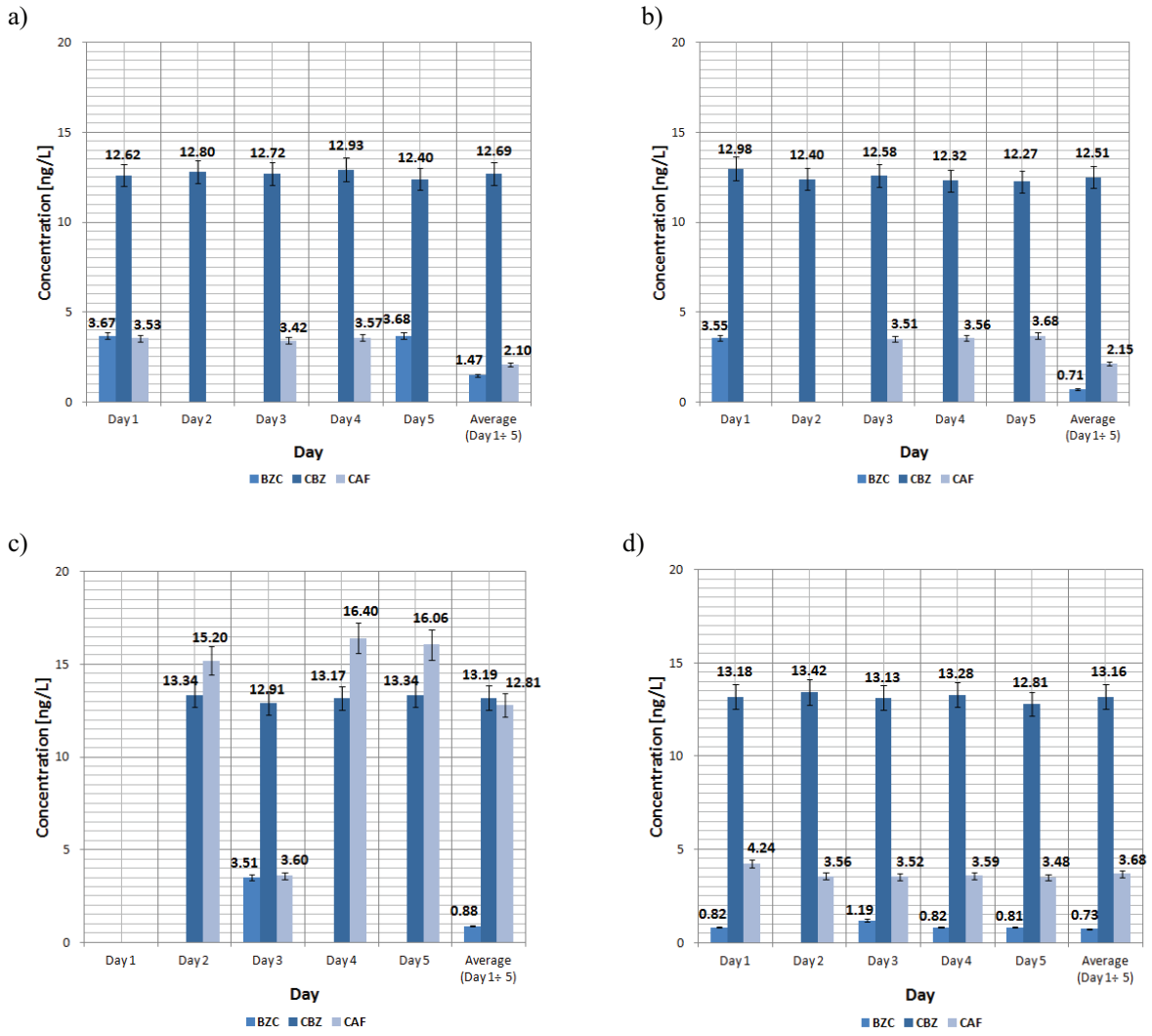


Fig. 1. Daily concentrations of selected pharmaceuticals in (a) paddling pool, (b) jacuzzi, (c) water slide (water slide was closed and excluded from use in the first day of research) and (d) sports pool.

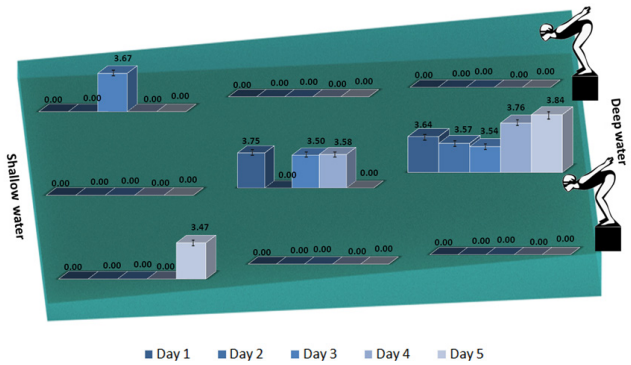


Fig. 2. Map of daily changes in BZC concentrations in various points of sports basin (ng/L).

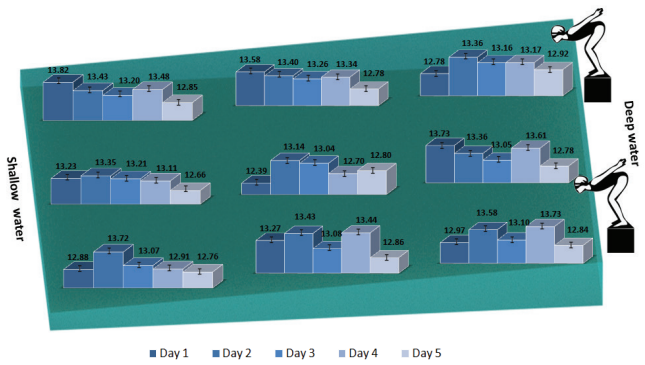


Fig. 3. Map of daily changes in CBZ concentrations in various points of sports basin (ng/L).

jacuzzi and water slide, the variability of concentration levels in different locations were not significant. The variability of the result depending on the location of the collection point in the sports pool was probably due to the size of this basin.

Clearly visible is that benzocaine occurred everyday in sports pool but only in one specific point of basin (Fig. 2). The mean value of its concentration in this point was 3.67 ng/L, while the mean value from the all points was

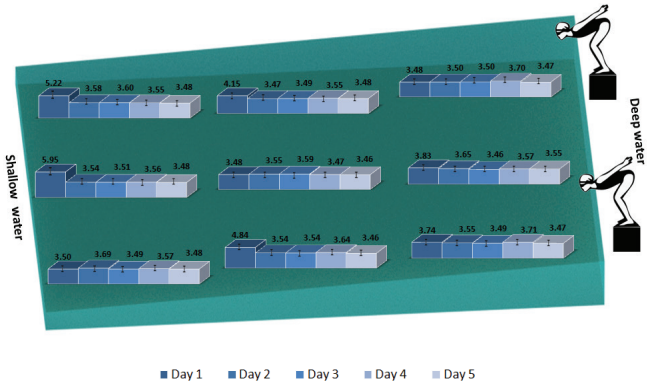


Fig. 4. Map of daily changes in CAF concentrations in various points of sports basin (ng/L).

0.81 ng/L. In other points of this pool, it was rarely detected (Fig. 2). The highest concentration of benzocaine in sports pool occurred in the last day of the research. That day, its concentrations were in scoped from <0.75 to 3.84 ng/L. Also relatively high dispersions of caffeine concentrations were observed (Fig. 4). For example, the caffeine concentration measurements ranged in the first day from 3.58 to 5.95 ng/L. The distribution of pharmaceuticals concentration levels in sports pool (mainly the distribution of benzocaine concentrations) confirmed that – as it was proved by Wyczarska-Kokot et al. [41] – water flow through the basin may cause the occurrence of "dead zones" that do not take part in the circulation. This may encourage the accumulation of pollutants in individual points.

As swimming pools are sourced from tap water, it can be expected that the pharmaceuticals are introduced into the swimming pool during filling the basins. However, the chromatography analysis of tap water did not confirm the occurrence of any tested pharmaceuticals. Caffeine, benzocaine and carbamazepine were below the LOQ in all of the tap water samples. This implies that the compounds present in the swimming pool water have been introduced by the swimmers. The selected pharmaceutical compounds are commonly found in commercial products that are likely to be used by the users of the pool and their probable source in swimming pool water is the excretion of body fluids. The carried out analysis on tap water samples confirmed that filling water do not contribute to the occurrence of pharmaceuticals in tested swimming pools and it excluded tap water as a possible source of detections pharmaceutical compounds in investigated swimming pool basins.

The differences in measured concentrations for different points of sampling presented in Figs. 2–4 result from the type of swimming pool hydraulic system. Water is constantly entering the tested swimming pool basin by the so-called vertical system. It means that the inflow of water takes place from the bottom by a lot of small special pool bottom nozzles, while the outflow through the overflow gutters is located along the two longer edges of the pool basin. This solution of water flow in a swimming pool basin causes that the water is not perfectly mixed inside the basin [41,42]. There are even so-called "dead zones" in which it is possible that water does not mix at all. They can occur, for example, in the corners of the basin or along the edge where there are no overflow gutters [41]. The map of daily changes in BZC (Fig. 2) best shows the possible locations of "dead zones" in the pool under study. BZC distribution points (in corners and along edges that are not equipped with overflow gutters) are located exactly in the zones that are usually supposed to be "dead zones". After the probable BZC bringing by one of swimmer, as a result of good water flow through some zones, no BZC was observed at most of the points (it floated to the overflow gutter, then to the balance tank and water treatment installation). However, in the "dead zones", BZC gathered and accumulated. The map of daily changes in BZC concentrations at various points in a sports basin (Fig. 2) may indicate that contamination of the examined pool by BZC was a single accident. Perhaps this compound was introduced once and then quickly removed in the water purification installation. As in the most of points it was not found, the coming back water flowing from the treatment installation did not contain BZC.

On the other hand, maps of daily changes in CAF and CBZ show that these two compounds are constantly present in the basin pool. Every day, at all sampling points, the presence of these compounds was noted. This may indicate that the pool water treatment system is not able to remove them from water. At some points, concentration of these compounds was almost unchanged. This confirms the conjecture of bad water mixing in these places. Some fluctuations in the concentration of CAF and CBZ in other points suggest that these compounds are systematically introduced into swimming pool by users.

However, the vertical hydraulic system, that is used in the tested swimming pool in this research, has been proven to be the best currently used in swimming pools [42]. Probably, in pools equipped with a different type of flow (horizontal system or skimmer system), the degree of mixing water in the basin is even smaller than in vertical system and it seems that if measurements of micropollutants concentrations are carried out in these types of swimming pool basins, the differences in different points of basin will be even greater than in the presented work.

4. Summary and conclusions

- The study has documented the impact of basin function on the concentration levels of particular micropollutants. The highest concentration of both carbamazepine and caffeine occurred in water slide. The highest concentration level of benzocaine was measured in paddling pool. The lowest values of carbamazepine and benzocaine concentrations were observed in jacuzzi, while the lowest concentration of caffeine was detected in paddling pool.
- Depending on the point of sampling in the sports basin, the measured concentrations were different. Benzocaine did not even appear in some points, while in others it was present in relatively high concentrations. In case research performed in big-sized swimming pool, there is a necessity to collect samples from various points of basin in order to obtain reliable and the actual results.
- The differences in measured concentrations for different sampling points result from the specificity of the swimming pools' hydraulic system: the occurrence of both "dead zones" and zones of good water mixing.

- No impact of water quality parameters on the levels of tested pharmaceuticals has been shown in this research.
- The frequent occurrence of carbamazepine and caffeine indicates that the conventional systems of water treatment used in examined swimming pools are not effective in removing these pharmaceuticals. To remove pharmaceuticals from swimming pools effectively, frequent water refill or new treatment technologies shall be considered. Further research should assess whether their costs are justified.
- The high variability of pharmaceuticals concentrations depending on different aspects shows that the topic of this research is very complex and confirms the need for further research.

Acknowledgment

This work was supported by Research Funds for Young Researchers awarded to the Institute of Water and Wastewater Engineering of the Silesian University of Technology (No. BKM/554/RIE-4/2017).

References

[1] K. Krümmerer, Ed., Pharmaceuticals in the Environment: Sources, Fate, Effects, and Risks, 3rd ed., Springer, Berlin, 2008.
[2] K. Krümmerer, The presence of pharmaceuticals in the environment due to human use-present knowledge and future challenges, J. Environ. Manage., 90 (2009) 2354–2366.
[3] D. Taylor, T. Senac, Human pharmaceutical products in the environment - the "problem" in perspective, Chemosphere, 115 (2014) 95–100.
[4] W.C. Li, Occurrence, sources, and fate of pharmaceuticals in aquatic environment and soil, Environ. Pollut., 187 (2014) 193–201.
[5] L. Cizmas, V.K. Sharma, C.M. Gray, T.J. McDonald, Pharmaceuticals and personal care products in waters: occurrence, toxicity, and risk, Environ. Chem. Lett., 13 (2015) 381–394.
[6] S.C. Weng, P. Sun, W. Ben, C.H. Huang, L.T. Lee, E.R. Blatchely, The presence of pharmaceuticals and personal care products in swimming pools, Environ. Sci. Technol. Lett., 12 (2014) 495–498.
[7] T.L. Teo, H.M. Coleman., S.J. Khan, Occurrence and daily variability of pharmaceuticals and personal care products in swimming pools, Environ. Sci. Pollut. Res., 23 (2016) 6972–6981.
[8] Y. Ekowati, G. Buttiglieri, G. Ferrero, J. Valle-Sistac, M.S. Diaz-Cruz, D. Barceló, M. Petrovic, M. Villagrasa, M.D. Kennedy, I. Rodríguez-Roda, Occurrence of pharmaceuticals and UV filters in swimming pools and spas, Environ. Sci. Pollut. Res. Int., 23 (2016) 14431–14441.
[9] L.M. Suppes, C.H. Huang, W.N. Lee, K.J. Brockman, Sources of pharmaceuticals and personal care products in swimming pools, J. Water Health, 15 (2017) 829–833.
[10] A.P. Dufour, O. Evans, T.D. Behymer, R. Cantú, Water ingestion during swimming activities in a pool: a pilot study, J. Water Health, 4 (2006) 425–430.
[11] F.A. Caliman, M. Gavrilescu, Pharmaceuticals, personal care products and endocrine disrupting agents in the environment-a review, Clean Soil Air Water, 37 (2009) 277–303.
[12] T.A. Ternes, M. Meisenheimer, D. McDowell, F. Sacher, H.-J. Brauch, B. Haist-Gulde, G. Preuss, U. Wilme, N. Zulei-Seibert, Removal of pharmaceuticals during drinking water treatment, Environ. Sci. Technol., 36 (2002) 3855–3863.
[13] L.K. Blackstock, W. Wang, S. Vemula, B.T. Jaeger, X.-F. Li, Sweetened Swimming Pools and Hot Tubs, Environ. Sci. Technol. Lett., 4 (2017) 149–153.
[14] P. Dalkmann, et al., Accumulation of pharmaceuticals, enterococcus, and resistance genes in soils irrigated with wastewater for zero to 100 years in Central Mexico, PLoS One, 7 (2012) e45397.
[15] T.L. Teo, H.M. Coleman, S.J. Khan, Chemical contaminants in swimming pools: occurrence, implications and control, Environ. Int., 76 (2015) 16–31.
[16] P. Bottoni, L. Bonadonna, S. Caroli, G. Zaray, Emerging issues on degradation by-products deriving from personal care products and pharmaceuticals during disinfection processes of water used in swimming pools, Microchem. J., 112 (2014) 13–16.
[17] A. Zhang, Y. Li, Y. Song, J. Lv, J. Yang, Characterization of pharmaceuticals and personal care products as N-nitrosodimethylamine precursors during disinfection processes using free chlorine and chlorine dioxide, J. Hazard. Mater., 276 (2014) 499–509.
[18] R. Shen, S.A. Andrews, Demonstration of 20 pharmaceuticals and personal care products (PPCPs) as nitrosamine precursors during chloramine disinfection, Water Res., 45 (2011) 944–952.
[19] S.T. Glassmeyer, A. Shoemaker, Effects of chlorination on the persistence of pharmaceuticals in the environment, Bull. Environ. Contam. Toxicol., 74 (2005) 24–31.
[20] K. Kawabata, K. Sugihara, S. Sanoh, S. Kitamura, S. Ohta, Photodegradation of pharmaceuticals in the aquatic environment by sunlight and UV-A, -B and -C irradiation, J. Toxicol. Sci., 38 (2013) 215–223.
[21] A.B. Boxall, M.A. Rudd, B.W. Brooks, D.J. Caldwell, K. Choi, S. Hickmann, E. Innes, K. Ostapyk, J.P. Staveley, T. Verslycke, G.T. Ankley, K.F. Beazley, S.E. Belanger, J.P. Berninger, P. Carriquiriborde, A. Coors, P.C. Deleo, S.D. Dyer, J.F. Ericson, F. Gagné, J.P. Giesy, T. Gouin, L. Hallstrom, M.V. Karlsson, D.G. Larsson, J.M. Lazorchak, F. Mastrocco, A. McLaughlin, M.E. McMaster, R.D. Meyerhoff, R. Moore, J.L. Parrott, J.R. Snape, R. Murray-Smith, M.R. Servos, P.K. Sibley, J.O. Straub, N.D. Szabo, E. Topp, G.R. Tetreault, V.L. Trudeau, G. Van Der Kraak, Pharmaceuticals and personal care products in the environment: what are the big questions?, Environ. Health Perspect., 12 (2012) 1221–1229.
[22] J.M. Brausch, K.A. Connors, B.W. Brooks, G.M. Rand, Human pharmaceuticals in the aquatic environment: a review of recent toxicological studies and considerations for toxicity testing, Rev. Environ. Contam. Toxicol., 218 (2012) 1–99.
[23] L.H. Santos, A.N. Araújo, A. Fachini, A. Pena, C. Delerue-Matos, M.C. Montenegro, Ecotoxicological aspects related to the presence of pharmaceuticals in the aquatic environment, J. Hazard. Mater., 175 (2010) 45–95.
[24] A. Lempart, E. Kudlek, M. Dudziak, Identification of New Groups of Micropollutants in Swimming Pool Water, J. Kulczycka, Ed., Young Researchers' Innovative Ideas: Science Start-Ups in the Industry, Kraków, IGSMiE PAN, 2017, p. 91.
[25] A. Lempart, E. Kudlek, M. Dudziak, The Occurrence of Micropollutants from PPCPs Macro Group in Swimming Pool Water, Central European Conference ECOpole'17, 4–7 October, Abstracts, 2017, p. 25.
[26] E.J. van den Brandhof, M. Montforts, Fish embryo toxicity of carbamazepine, diclofenac and metoprolol, Ecotoxicol. Environ. Saf., 73 (2010) 1862–1866.
[27] G.V. Aguirre-Martínez. S. Buratti, E. Fabbr, A.T. DelValls, M.L. Martín-Díaz, Using lysosomal membrane stability of haemocytes in *Ruditapes philippinarum* as a biomarker of cellular stress to assess contamination by caffeine, ibuprofen, carbamazepine and novobiocin, J. Environ. Sci. (China), 25 (2013) 1408–1418.
[28] A. Bahlmann, J.J. Carvalho, M.G. Weller, U. Panne, R.J. Schneider, Immunoassays as high-throughput tools: monitoring spatial and temporal variations of carbamazepine, caffeine and cetirizine in surface and wastewaters, Chemosphere, 89 (2012) 1278–1286.
[29] H. Chen, J. Zha, X. Liang, Z. Wang, Effects of the human antiepileptic drug carbamazepine on the behavior, biomarkers, and heat shock proteins in the Asian clam *Corbicula fluminea*, Aquat. Toxicol., 155 (2014) 1–8.
[30] A. Kacperska, Plant Responses to Abiotic Stressors, J. Kopcewicz, S. Lewak, Eds., Plant Physiology, PWN, Warszawa, 2002, pp. 612–678 (in Polish).

[31] Z.H. Li, P. Li, M. Rodina, T. Randak, Effect of human pharmaceutical carbamazepine on the quality parameters and oxidative stress in common carp (*Cyprinus carpio* L.) spermatozoa, Chemosphere, 80 (2010) 530–534.
[32] G.K. McEvoy, Ed., AHFS Drug Information, in: Benzocaine, American Society of Health-System Pharmacists, Bethesda, 2007, pp. 2844–2845.
[33] United States Food and Drug Administration, Life-Threatening Side Effects with the Use of Skin Products Containing Numbing Ingredients for Cosmetic Procedures: Public Health Advisory, 2007. Available at: https://wayback.archive-it.org/7993/20170723000353/https://www.fda.gov/Drugs/DrugSafety/PostmarketDrugSafetyInformationforPatientsandProviders/ucm054718.htm.
[34] J.R. Shua-Haim, J.S. Gross, Methemoglobinemia toxicity from topical benzocaine spray, J. Am. Geriatr. Soc., 43 (1995) 590.
[35] A.J. González-Rodríguez, E.M. Gutiérrez-Paredes, A. Revert Fernández, E. Jordá-Cuevas, Allergic contact dermatitis to benzocaine: the importance of concomitant positive patch test results, Actas Dermosifiliogr., 104 (2013) 156–158.
[36] A. Jagoda, W. Żukowski, B. Dąbrowska, Investigations of the presence of caffeine in the Rudawa River, Kraków, Poland, Environ. Monit. Assess., 187 (2015) 566.
[37] J. Wu, J. Yue, R. Hu, Use of Caffeine and human pharmaceutical compounds to identify sewage contamination, Int. J. Environ. Eng., 2 (2010) 98–102.
[38] DIN 19643, Aufbereitung von Schwimm und Badebeckenwasser, Dusseldorf, 1997.
[39] Regulation of the Minister of Health of 9 November 2015 on the Requirements for Water in the Swimming Pools, Journal of Laws of the Republic of Poland No 2015 item 2016 (in polish).
[40] R. Seiler, S.D. Zaugg, J.M. Thomas, D.L. Howcroft, Caffeine and pharmaceuticals as indicators of waste water contamination in wells, Groundwater, 37 (1999) 405–410.
[41] J. Wyczarska-Kokot, A. Lempart, M. Dudziak, Chlorine Contamination in Different Points of Pool - Risk Analysis for Bather Health, Central European Conference ECOpole'17, 2017, pp. 41–42.
[42] F. Piechurski, Which system pays off? part 1 - Conditions for the design of pool water circulation installations (in Polish: Jaki system się opłaca cz. 1 – Warunki projektowania instalacji cyrkulacji wody basenowej), Pływalnie i baseny, 7 (2011) 88–95.