The Presence of Compounds from the Personal Care Products Group in Swimming Pool Water

Anna Lempart1*, Edyta Kudlek1, Marta Lempart1, Mariusz Dudziak1

1 Silesian University of Technology, Institute of Water and Wastewater Engineering, Konarskiego 18, 44-100 Gliwice, Poland
* Corresponding author’s e-mail: anna.lempart@polsl.pl

ABSTRACT
The global production of several thousands of Personal Care Products (PCPs) every year makes the release of PCPs to the environment an unavoidable by-product of a modernized lifestyle. Multiple studies have detected PCPs worldwide in various aquatic environments, including swimming pools. In the presented work, the concentrations of three selected compounds from the PCPs group were examined in 15 swimming pools with different functions. The aim of the study was to show the influence of various factors on the concentration levels of selected micropollutants. Two UV filters: BP-3 (oxybenzone), BP-8 (dioxybenzone) and one antioxidant BTH (dibutylhydroxytoluene) were selected for the research. The extraction of micropollutants from the swimming pool water matrix was carried out by Solid Phase Extraction (SPE). The extracts were analyzed using a gas chromatograph (GC) coupled to the mass detector (MS). BHT was the most common compound. Its concentration ranged from 3.8 ng/L to 5.5 ng/L. The most rarely occurring compound was BP-3. The concentration of this compound varied the most, from 18.5 ng/L to 1178.6 ng/L. BP-8 was present in 10 from 15 tested pools at the concentration level of 49.9–226.9 ng/L. The frequency of occurrence characterizing different micropollutants from PCPs group was higher in recreational pools than in sports pools. It was also observed that the applied water treatment technology may affect the presence of Personal Care Products in the swimming pool water. No impact of basic water quality parameters on the levels of tested pharmaceuticals has been shown in this research.

Keywords: swimming pools, personal care products, cosmetics, micropollutants, parabens, UV filters

INTRODUCTION
The group of Personal Care Products (PCPs) includes the compounds present in both personal hygienic items, which are necessities, and cosmetics, which are luxury goods solely used for beautification. It concerns products as diverse as for example colognes, deodorants, eye liners, lip glosses, lipsticks, lotions, nail polishes, powders, perfumes, shaving cream, moisturizers, talcum powders, toothpastes, sunscreens, soaps, fragrances, insect repellents, and shampoos. The personal-care industry is a massive field. According to the Personal Care Products Council, a trade association for the cosmetics and personal-care products industry that has more than 600 members, it generates more than $250 billion in annual retail sales, worldwide. The global production of several thousands of PCPs every year makes the release of PCPs to the environment an unavoidable by-product of a modernized lifestyle.

Multiple studies have detected PCPs worldwide in various aquatic environments such as surface waters, groundwater, drinking waters [Boyd et al. 2003; Cizmas et al. 2015; Ebele et al. 2017; Snyder et al. 2004; Yang et al. 2017] and more recently, swimming pool waters [Cuderman and Heath 2007; Ekowati et al. 2016; Giokas et al. 2004; Giokas et al. 2005; Lambropoulou et al. 2002; Lempart et al. 2017; Lopez-Darias et al. 2010; Regueiro et al. 2009; Suppes et al. 2017; Terasaki and Makino 2008; Vidal et al. 2010; Li et al. 2015; Zwiener et al. 2007]. Some compounds from the PCPs group may cause negative human health effects, mainly the allergic reactions, but also the endocrine or fertility disorders [Caliman and Gavrilescu 2009; Piao et al. 2014, Tavares et
al. 2009] and hormonal changes [Golden et al. 2005; Kunz et al., 2006; Kunz and Fent 2006; Ma et al., 2003; Morohoshi et al. 2005; Schlumpf et al. 2001; Suzuki et al. 2005]. For this reason, their presence in swimming pools, where users are directly exposed to them by three different routes: inhalation, absorption through the skin and ingestion, seems to be particularly worrying. Swimming is a popular leisure activity that can provide health benefits for the public. However, it turns out that the exposure to water in swimming pools may cause a number of health risks related to the chemical hazards caused i.a. by PCPs and the occurrence of their by-products. The PCPs of concern in swimming pool water include compounds with the ability to absorb UV radiation, which are the main component of sunscreen products and parabens that are widely applied as antimicrobial preservatives in cosmetics, pharmaceuticals and food, as well as active substances in antiperspirants and antidiarrheal products. The Personal Care Products detected so far in swimming pools are summarized in Table 1.

UV filters are the main components of sunscreens. They are composed of organic and inorganic compounds which absorb or reflect the UV light. Due to the mechanism of action, they can be divided into two basic groups: physical filters and chemical filters. The physical filters include titanium dioxide (TiO₂) and zinc oxide (ZnO). Their action is based on the scattering of radiation [Bojnarovicz and Bartnikowska 2014]. The chemical filters are organic compounds that have the ability to absorb the radiation. The common feature of all of them is the presence of numerous unsaturated bonds and moieties containing free electron pairs in the molecule. They absorb the energy of sunlight, turning it into the thermal energy. They commonly consist of aromatic compounds conjugated with carbonyl groups. The most commonly used are benzophenones, phenylbenzotriazoles and the derivatives of: p-aminobenzoic acid, p-methoxycinnamic acid, salicylic acid, camphor, dibenzylymethane and benzylidenecamphor [Bojnarovicz and Bartnikowska 2014]. Some sunscreen agents exhibit estrogenicity and antiandrogenicity [Kunz et al., 2006, Kunz and Fent, 2006; Ma et al., 2003; Morohoshi et al., 2005; Schlumpf et al., 2001; Suzuki et al., 2005]. There are also concerns about their potential carcinogenicity [Lowe 2006]. Certain sunscreen agents in aquatic matrices are degraded under the influence of sunlight and reaction with chlorine [Nakajima et al. 2009; Negreira et al. 2008; Rodil et al. 2009, Sakkas et al. 2003; Serpone et al. 2002; Virkutyte et al. 2012]. These transformations can cause the formation of by-products that may be more harmful than their parent compounds. [Díaz-Cruz and Barceló 2009; Giokas et al. 2007].

Parabens, a group of alkyl esters of p-hydroxybenzoic acid (PHBA), in general are moderately soluble in water and not volatile. Due to the active phenol hydroxyl groups, they can be easily transformed to mono- and di-chlorinated derivatives in chlorinated water [Terasaki et al. 2012; Westerhoff et al. 2005]. Therefore, during the disinfection of swimming pool water, they may form chlorinated parabens which are more stable in environment and more toxic than the corresponding parent parabens [Blédzka et al. 2014; Terasaki et al. 2009]. Both parabens and their chlorinated derivatives exhibit the endocrine-disrupting properties. They can modulate or disrupt the endocrine system and harm human health [Golden et al. 2005, Piao et al. 2014]. The association between the human exposure to parabens and adverse health outcomes has been shown in the epidemiological studies [Meeker et al. 2011; Savage et al. 2012]. PHBAs, due to their common presence in Personal Care Products, are the most sensitizing substances in contact.

In the presented work, the concentrations of three selected compounds from the PCPs group were examined in swimming pools with different functions. Two UV filters, BP-3 (oxybenzone), BP-8 (dioxbenzone) and one antioxidant BTH (dibutylhydroxytoluene) were selected for research. They are characterized in Table 2.

The aim of the study was to show the influence of various factors on the concentration levels of selected micropollutants.

MATERIALS AND METHODS

The PCPs listed in Table 2 are the target compounds in this study. The standards of high purity (BP-3 and BP-8 >98%, BHT >95%) were purchased from Sigma Aldrich. The cartridges used for Solid Phase Extraction were Supelclean™ ENV1-18 SPE Tube from Sigma Aldrich filled with non-polar adsorbent C18 (octadecyl bonding). Organic solvents: methanol and acetonitrile of purity grade >99.8% and >99.5%, respectively, by Avantor Performance Materials Poland S.A. were also applied to Solid Phase Extraction. A gas chromatograph coupled with a mass detector (GC-MS) with electron ionization (EI) by PER-
LAN Technologies, model 7890B, was used for the chromatographic analysis.

The water samples of 100 mL volume were collected from eight swimming centers (B1-B8) and one hotel (B9_H) located in Poland within 6 months (June-November 2017). Swimming center B1 includes four different pools: Sports Pool (B1_S), Jacuzzi (B1_J), Paddling Pool (B1_P) and Water Slide (B1_W). Swimming centers B2-B4 include Sports Pools (B2_S, B3_S, B4_S) and Jacuzzis (B2_J, B3_J, B4_J). Each of swimming centers B5-B7 includes only one Sports Pool (B5_S, B6_S, B7_S), while B8 includes only one Paddling Pool for children to learn to swim (B8_P). In total, water samples were collected from 15 different indoor pools: 7 sports pools and 8 recreational pools (including 4 Jacuzzis, 2 paddling pools, 1 water slide pool and 1 hotel’s pool). They are summarized in Table 3. The basic physicochemical parameters (pH, absorbance UV in
The collected water samples were subjected to the chromatographic analysis to determine the concentrations of selected micropollutants in different types of swimming pools. The chromatographic analysis and the sample preparation were carried out in accordance with the developed analytical procedure presented in the paper [Lempart et al. 2018], which enables the qualitative and quantitative analysis of micropollutants from the group of Pharmaceutical and Personal Care Products with satisfactory reproducibility and accuracy. The obtained recovery values ensure the possibility of full quantitative control of the examined micropollutants in samples collected from swimming pools.

Depending on the point of sampling, the measured concentrations of the micropollutants may be different. Therefore, the samples were collected from 7 different points of each swimming pool and then mixed together. Every representative sample prepared in this way was extracted using the SPE methodology and analyzed using the GC-MS three times in order to minimize the potential analytical mistakes. The presented in paper concentrations of compounds are the arithmetical mean of these results.

The Limits Of Quantification (LOQ) of the tested pharmaceuticals were 0.85 ng/L for BHT, 0.67 ng/L for BP-3, and 0.74 ng/L for BP-8, respectively. The values of the Coefficient of Variation (CV) that is a measure of the repeatability of the results, do not exceed 3% which confirms the high repeatability of the conducted measurements.

The details of the analytical procedure are presented in Table 4.

### Table 2. The characteristics of selected compounds

<table>
<thead>
<tr>
<th>Name</th>
<th>Structural formula</th>
<th>Chemical formula</th>
<th>CAS Number</th>
<th>Molar mass [g/mol]</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxybenzone (BP-3)</td>
<td><img src="image" alt="Structure" /></td>
<td>C_{14}H_{12}O_3</td>
<td>131-57-7</td>
<td>228.25</td>
<td>Personal Care Products / in sunscreens, hair sprays, and nail polishes as an ultraviolet light absorber and stabilizer/</td>
</tr>
<tr>
<td>Dioxibenzene (BP-8)</td>
<td><img src="image" alt="Structure" /></td>
<td>C_{14}H_{12}O_4</td>
<td>131-53-3</td>
<td>244.25</td>
<td>Personal Care Products / in sunscreen to block UVB and short-wave UVA rays/</td>
</tr>
<tr>
<td>Dibutylhydroxytoluene (BHT)</td>
<td><img src="image" alt="Structure" /></td>
<td>C_{15}H_{24}O_3</td>
<td>128-37-0</td>
<td>220.36</td>
<td>Personal Care Products / as an antioxidant/</td>
</tr>
</tbody>
</table>

### Table 3. The characteristics of tested swimming pools and parameters of water samples

<table>
<thead>
<tr>
<th>Name</th>
<th>Type</th>
<th>Treatment</th>
<th>pH</th>
<th>UV_{254}</th>
<th>Conductivity</th>
<th>TOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1_S</td>
<td>Sport pool</td>
<td>Yes</td>
<td>7.20</td>
<td>0.032</td>
<td>1.095</td>
<td>3.82</td>
</tr>
<tr>
<td>B1_J</td>
<td>Jacuzzi</td>
<td>Yes</td>
<td>6.83</td>
<td>0.018</td>
<td>1.2708</td>
<td>1.52</td>
</tr>
<tr>
<td>B1_P</td>
<td>Paddling pool</td>
<td>Yes</td>
<td>7.31</td>
<td>0.027</td>
<td>0.3985</td>
<td>2.97</td>
</tr>
<tr>
<td>B1_W</td>
<td>Water slide</td>
<td>Yes</td>
<td>7.52</td>
<td>0.030</td>
<td>1.1537</td>
<td>3.65</td>
</tr>
<tr>
<td>B2_S</td>
<td>Sport pool</td>
<td>Yes</td>
<td>6.90</td>
<td>0.007</td>
<td>1.960</td>
<td>0.69</td>
</tr>
<tr>
<td>B2_J</td>
<td>Jacuzzi</td>
<td>Yes</td>
<td>6.97</td>
<td>0.006</td>
<td>1.196</td>
<td>0.89</td>
</tr>
<tr>
<td>B3_S</td>
<td>Sport pool</td>
<td>Yes</td>
<td>6.73</td>
<td>0.012</td>
<td>0.7966</td>
<td>3.49</td>
</tr>
<tr>
<td>B3_J</td>
<td>Jacuzzi</td>
<td>Yes</td>
<td>7.00</td>
<td>0.005</td>
<td>0.9541</td>
<td>0.79</td>
</tr>
<tr>
<td>B4_S</td>
<td>Sport pool</td>
<td>Yes</td>
<td>5.99</td>
<td>0.033</td>
<td>0.8367</td>
<td>2.99</td>
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<tr>
<td>B4_J</td>
<td>Jacuzzi</td>
<td>Yes</td>
<td>8.23</td>
<td>0.050</td>
<td>0.6032</td>
<td>4.89</td>
</tr>
<tr>
<td>B5_S</td>
<td>Sport pool</td>
<td>Yes</td>
<td>7.29</td>
<td>0.021</td>
<td>1.2160</td>
<td>0.83</td>
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<tr>
<td>B5_J</td>
<td>Jacuzzi</td>
<td>Yes</td>
<td>7.69</td>
<td>0.126</td>
<td>0.6663</td>
<td>7.66</td>
</tr>
<tr>
<td>B6_S</td>
<td>Sport pool</td>
<td>Yes</td>
<td>6.69</td>
<td>0.028</td>
<td>2.169</td>
<td>9.09</td>
</tr>
<tr>
<td>B6_J</td>
<td>Jacuzzi</td>
<td>Yes</td>
<td>6.99</td>
<td>0.048</td>
<td>1.9978</td>
<td>28.07</td>
</tr>
<tr>
<td>B7_S</td>
<td>Paddling pool</td>
<td>Yes</td>
<td>5.57</td>
<td>0.048</td>
<td>0.6032</td>
<td>4.03</td>
</tr>
<tr>
<td>B7_P</td>
<td>Paddling pool</td>
<td>Yes</td>
<td>7.33</td>
<td>0.014</td>
<td>0.4431</td>
<td>4.03</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

The Figure 1 shows the concentrations of selected micropollutants in different types of swimming pool basins (Sports Pool, Jacuzzi, Paddling Pool and Water Slide) in one swimming center, B1. Both BHT and BP-8 were present in all types of basins in this swimming center. The concentration levels of BP-8 varied from 49.9 to 53.2 ng/L, while the concentration levels of BHT ranged 4.2–5.0 ng/L. BP-3 occurred in two pools in the concentrations higher than value of Limit of Quantification, 18.5 ng/L in Paddling Pool and 51.9 ng/L in Sports Pool. In Jacuzzi and Water Slide Pool, its concentration was lower than LOQ_BP-3 0.67 ng/L.

The Figure 2 presents the concentrations of selected micropollutants in the same types of basins in different swimming pool centers. The concentration of BHT (Fig. 2 a) fluctuated slightly, in Sports Pools it changed 3.8–5.0 ng/L, in Jacuzzi it varied 4.1–4.7 ng/L and in others (including Paddling Pools, Water Slide and Hotel’s Pool), it ranged 4.2–5.5 ng/L. The concentration of BP-3 (Fig. 2 b) in Sports Pools differed from 51.9 ng/L to 1178.6 ng/L, only in one Jacuzzi it was identified at value higher than limit of quantification (LOQ_BP-3 = 0.67 ng/L) and it did not occur in other pools. The concentration of BP-8 (Fig. 2 c) fluctuated considerably in ranges 53.2–86.9 ng/L in Sports Pools, 49.9–88.9 ng/L in Jacuzzis, 51.9–226.9 ng/L in others.

The concentration level of BP-8 in this study differs a lot from the concentration range by Ekowati (Ekowati et al. 2016). The lowest value measured in this study was 49.9 ng/L while Ekowati presented 21.6 ng/L as the highest concentration of BP-8 in his work. The concentration of BP-3 in this study fluctuated considerably, which confirms the previous research by Lambropoulou et al., Giokas et al., Cuderman and Heath, Zwiener et al., Vidal et al. and Ekowati et al. In the afore-mentioned works, the concentration of BP-3 varied greatly, from 4.2 ng/L to 3300 ng/L. This paper also shows the strong variability of BP-3 concentration in the swimming pool water. The concentration of BHT in swimming pool water has never been tested before. In this study, BHT was the most common compound. It was present in 13 tested swimming pools. If present, its concentration fluctuated slightly around the mean value 4.4 ng/L. The most rarely occurring compound was BP-3 (Figure 3), which was the most frequently tested Personal Care Product in previous works.

<table>
<thead>
<tr>
<th>Table 4. The details of the analytical procedure</th>
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<tbody>
<tr>
<td>Extraction conditions</td>
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<tr>
<td>-----------------------</td>
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<tr>
<td></td>
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<tr>
<td>Chromatograph parameters</td>
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</tbody>
</table>

**Figure 1.** The concentration of BHT, BP-3 and BP-8 in different swimming pools in centre B1.
The Figure 4 shows frequency of appearance the different micropollutants from PCPs group in swimming pools categorized by the type of pool: Sports and Recreational (including Jacuzzi, Paddling Pool, Water Slide and Hotel’s Pool).

CONCLUSIONS

It was demonstrated that the concentration level of micropolllutants present in swimming pool depends on the kind of compound and the type of both swimming pool basin and the swimming pool center. Usually, the concentrations of each compound in different pool basins within a single swimming pool centre were similar. The concentrations of UV filters vary a lot in different swimming pool centers, while the concentration of antioxidant fluctuated slightly around the mean value.

The frequency of occurrence of the different micropolllutants from PCPs group was higher in the recreational pools than in the sports pool. No impact of basic water quality parameters on the levels of tested pharmaceuticals has been proven in this research.

It was also concluded that the applied water treatment technology may affect the presence of the Personal Care Products in the swimming pool water. In this study, neither the type of filtra-
tion bed layer nor the disinfection support technology, were analyzed. However, the high variability of concentrations of the tested PCPs suggests that some processes in pool water treatment installations may cause the decomposition or transformation of some compounds. This is particularly indicated by the absence of the tested micropollutants in pools B6 and B7.

Acknowledgements

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