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Toxicology Classification of Pool Water Quality in Relation to Selected Pollutant Fractions Present in Washings Samples †

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Abstract: The aim of the study is to determine the fractional share of organic pollutants in washings samples, collected after pressure filters washing. The evaluation of the physicochemical and toxicological quality of raw washings, fraction <200 kDa, <30 kDa and <300 Da has been presented. Separation of selected fractions was carried out with the participation of a multistage pressure membrane system using ultra- and nanofiltration. The physicochemical analysis was conducted based on the total organic carbon (TOC) concentration, dissolved organic carbon, and total carbon. The toxicological classification of isolated fractions was also prepared using the percentage of toxicity effects obtained in commercial bioassays—Microtox® and Artoxkit M. The concentration of TOC in the analyzed samples of raw washings was ranged from 2.50 to 11.00 mgC / L. The presented study showed a significant share of the organic pollutants fraction with a molar weight below 300 Da in the examined washings (the TOC was from 0.71 to 1.48 mgC/L). No correlation was observed between the concentration of TOC and the percentage of toxic effect. Screening toxicity tests can be a signal of swimming pool water quality; but they need to be extended with additional test organisms or observations of more morphological parameters of these organisms.

Keywords: swimming pool water; types of pools; total organic carbon (TOC); percentage toxic effect (PE); inhibition of bioluminescence; survival test of individuals; molecular weight fractions; molecular weight cut – off (MWCO); ultrafiltration; nanofiltration

1. Introduction

Organic pollutants introduced by the users are the main factor causing a significant deterioration of water quality in the pool basins. They mainly include the products of human metabolism, such as sweat and urine, which are inherently associated with physical activity, but also cosmetics ingredients or metabolites of pharmaceuticals [1–3].

The high reactivity of anthropogenic contamination was observed in the presence of chemical agents used for disinfection. The disinfection by-products (DBPs) formed as a result of these reactions constitute an increasingly widely studied problem [3–5]. The large interest in the DBPs group is related to their potentially harmful effects on the human body [6,7]. The beds with granular filling currently used in the pool water treatment systems are not completely selective in relation to

compounds from the group of DBPs. It is estimated that up to 30% of organic pollutants are washed out during the filtration process, getting into the purified water supplying the basin [3,8,9].

Most of the DBPs occurring in the pool water environment are characterized by molecular weight below 1000 g/mol [3,7]. The consequence of this is an increased ability to penetrate DBPs into the organisms of pool users [10,11]. Although the concentrations recorded in the examined pool water samples are often below 1 mg/L, the presence of DBPs is still detrimental to the bathers [12]. The production of enzymes that work in a way that causes oxidative stress in the cells of living organisms by DBPs has been confirmed [6]. Numerous studies in the field of pool water quality assessment using toxicological tests confirmed genotoxic, cytotoxic and mutagenic properties of DBPs [6,7,12].

Analysis of the contribution of selected pollutant fractions in pool water is particularly important in the light of reports on their genotoxic properties, which increase with decreasing molecular mass [5,7,8]. The highest genotoxicity is observed for compounds with a weight below 200 μg/mol [3]. For example, Glauner specifies a share of fraction> 1000 g/mol for 14%, share of fraction in the range of 200 ÷ 1000 g/mol as 54%, and fraction below 200 g/mol as 32% [7], which proves a significant share of the smallest fraction in the pool water environment.

Since genotoxicity and cytotoxicity evaluation methods require an access to specialized materials and reagents, their implementation generates high costs [13–15]. It is necessary to attempt to use the less sophisticated methods of toxicity evaluation, that would be of a screening nature and would allow for a preliminary assessment of samples quality before proceeding to more advanced analyzes. Tools that are commonly used for these purposes are acute toxicity tests for bioluminescence inhibition of *Aliivibrio fischeri* bacteria or survival of crustaceans—*Artemia franciscana (salina)* or *Daphnia magna* [14,16].

From the point of view of the pool water quality assessment, the concentration of carbon compounds, determined by the concentration of TOC, is particularly important. The TOC parameter shows a high correlation with the concentration of DBPs in samples of water subjected to chlorination processes [3,17]. Therefore, it can be information about the share of anthropogenic pollution in pool water samples.

The aim of the study is to determine the fractional share of organic pollutants in pool water samples taken from the installation of different types of pools of various purposes (toddler's pool, swimming pool, hot tub). The analyzes presented were carried out on the samples of waste streams—washings, collected after pressure filters rinsing. The evaluation of the physicochemical and toxicological quality of raw washings, fraction <200 kDa, <30 kDa and <300 Da has been presented. Separation of selected fractions was carried out with the participation of a multistage pressure membrane system using ultra- and nanofiltration. The physicochemical analysis was conducted based on the selected parameters—TOC concentration, dissolved organic carbon (DOC) and total carbon (TC). The toxicological classification of isolated fractions was also prepared using the percentage of toxicity effects obtained in commercial bioassays—Microtox® and Artoxkit M.

2. Methods

2.1. The subject of the study

The subject of the study was the washings collected independently of the three water treatment systems - a toddler's pool, swimming pool and hot tub. The washings were selected on the basis of preliminary tests, due to the large variation in the quality and quantity of pollutants present in them, which also circulate throughout the pool water treatment systems [18]. The washing samples were collected twice for each of the presented types of pools

An integral element of the analyzed systems are multilayer pressure filters (quartz sand with different granulation) with an activated carbon layer. The filter in the toddler's pool system has a filtration area of 2.01 m^2 and in the hot tub filtration system, there are 0.65 m^2. In turn, two filters with a filtration area of 2.54 m^2 are present in the system of the swimming pool, each. The filtration of water in each filter is carried out at a speed of 30 m/h. The washings samples were collected in

batches during the rinsing of the beds (in the evening), through the drain valves that drain the washing water to the overflow channel, and then to the sanitary sewage system. Washing of filtration beds (with compressed air and water) depends on the pressure loss during the filtration process, every 24 or 48 hours. The water for rinsing the beds is drawn from compensating tanks, where the pool water losses are supplemented with water from the municipal water supply network.

2.2. Fractionation of pollutants in a multistage system

Flat ultra- and nanofiltration membranes from Osmonics Inc. (USA), differing in the scope of the separation, the so-called molecular weight cut-off (MWCO) and the type of membrane-forming material were used for the fractionation of pollutants in the washings. A brief description of the membranes is presented in Table 1.

Table 1. Membrane characteristics.

Process	Membrane symbol	Membrane material	MWCO, Da	Operating pressure TMP, MPa
UF I	YMV53001	Polyvinylidene difluoride (PVDF)	200,000	0.2
UF II	YMV33001	Polyvinylidene difluoride (PVDF)	30,000	0.2
NF	YMHLSP3001	Polyamide—TFC	300—150	1.0

The membranes were placed in a steel filter cell with a volume of $3.80 \cdot 10^{-4}$ m^3, where the active filtration surface of the membrane is $38.5 \cdot 10^{-4}$ m^2. The filtrations were conducted in a one-way system (dead-end). The fractionation processes were carried out in UF I – UF II – NF multistage systems, according to the scheme shown in Figure 1. The feed for the first stage of filtration was made up of raw washings. The permeate obtained after UF I was used as the feed for UF II. The permeate after the second stage of ultrafiltration was used as a feed in the nanofiltration process. As part of the presented work, the focus was only on the physicochemical quality and toxicity classification of protected samples of raw washings and permeates.

2.3. Analysis of the physicochemical quality of the separated pollutant fractions

The values of selected physicochemical parameters were analyzed in the morning hours, in the washings secured in the previous evening. The concentrations of TC, organic carbon (TOC) and dissolved carbon (DOC) were determined in the samples of washings and/or permeate (after 0.45 μm filtration, PVDF syringe filter) using a TOC—L series analyzer using catalytic oxidation by combustion at 680°C (Shimadzu).

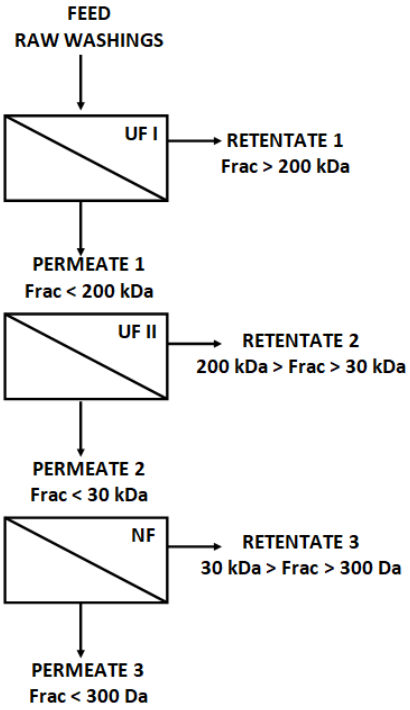

Figure 1. Fractionation (Frac) scheme of washings from pool water installations by membrane filtration.

2.2. Classification of toxicity of the obtained pollutants fractions

The toxicity classification of the examined samples was based on the average toxicity values obtained in the acute toxicity tests—Microtox® and Artoxkit M.

Toxicity analysis using the Microtox® test was carried out according to the MicrotoxOmni Screening. Test procedure in the Microtx Model 500 (Tigret) analyzer, acting as both an incubator and a photometer. Percent inhibition versus the control sample not subject to the potential toxicant in washings and permeates samples was measured after 5- and 15-minutes exposure time. The toxicity effect was determined as the percentage of bacterial bioluminescence inhibition E, %.

At the same time, the toxicity of the samples was assessed based on *Artemia salina* crustaceans larvae mortality test in accordance with ASTM E1440—91 (2012) [19]. The number of dead and/or immobile organisms was determined after 24 and 48 h of the test duration. A toxicity effect E, % was calculated for each sample of washings, permeate and control sample constituting brine solution for crustaceans breeding.

The toxicity effect E, % for the presented biotests was determined from the relationship (1):

$$E = \frac{100 \cdot (E_C - E_T)}{E_C}, \% \quad (1)$$

where the observed effect for the control sample was determined as E_C, and E_T is the effect observed for the test sample (washings, permeate).

The system presented in Table 2 [20], which is based on the determination of the so-called PE, is used for toxicity classification. The analyzed value is the average of both bioassays (for the second measurement: 15 min for the Microtox® test and 48 h for the Artoxkit M).

Table 2. Toxicity classification system [20].

PE	Class	Toxicity
≤ 20%	I	No acute hazard
20 ≤ PE ≤ 50%	II	Slight acute hazard

$50 \leq PE < 100\%$	III	Acute hazard
PE = 100%[1]	IV	High acute hazard

[1] At least in one bioassay.

Before the bioassays were carried out, the samples of raw washings were dechlorated (free chlorine disappearance in 72 h) and control measurements of chlorine concentration were made, which did not exceed 0.10 $mgCl_2/L$.

The statistical elaboration of the results of the toxicological analysis was made on the basis of the data analysis package in Microsoft Excel. The mean and standard deviation values were calculated as shown in the figures (Figure 2 – Figure 4).

3. Results and Discussion

The samples taken from the toddler's pool were characterized by a TC concentration in the range from 11.01 to 10.76 mgC/L. As a result of the multistage filtration, the TC concentration was lowered to the range from 4.65 to 1.93 mgC/L (Frac <300 Da). The concentration of DOC in raw washings was between 1.82 ± 0.18 mgC/L and 4.42 ± 0.19 mgC/L for sampling 1 and 2, respectively. In turn, the concentration of TOC was 6.32 ± 0.07 mgC/L and 5.95 ± 0.08 mgC/L (Figure 2). The TOC values in the successively separated fractions decreased. The concentration of TOC in the permeate after nanofiltration was 1.48 ± 0.05 and 0.71 ± 0.32 mgC/L (Figure 2).

Based on the percentage of toxicity, the samples of raw washings were classified as having a low toxic hazard (PE values of 35.70 ± 4.53% and 31.62 ± 4.80%). The highest PE value was recorded in the fraction below 30 kDa. The samples from the first sampling (Figure 2a) were classified as having a severe threat to the test organisms (50.65 ± 8.51%). In turn, the samples from the second sampling from the toddler's pool system were characterized by a percentage toxicity effect of 35.70 ± 0.19%. In addition, the first of the separated fractions (Frac <200 kDa) in the samples from sampling 2 showed a negative PE value, which was caused by strong stimulation of bacterial bioluminescence in the Microtox® test and low mortality of *A. salina* individuals in contact with this fraction (Figure 2b).

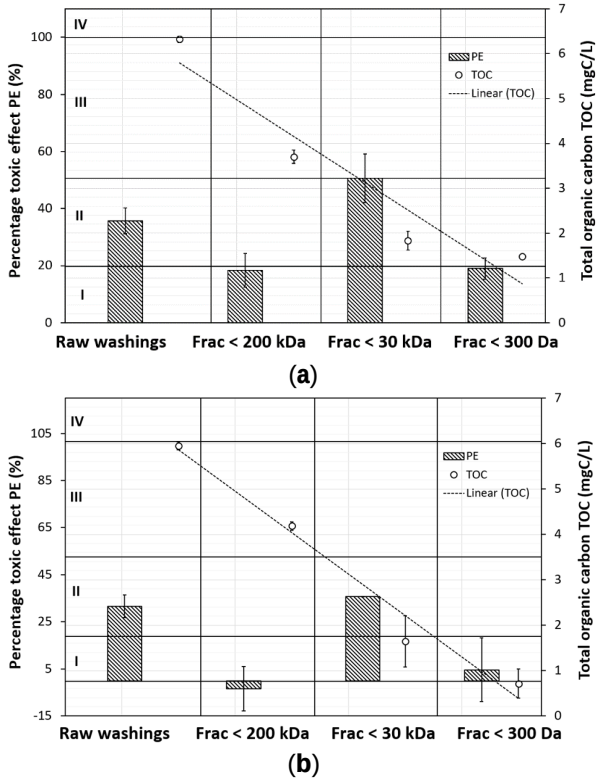

Figure 2. Values of TOC and PE in raw washings and separated fractions, samples were taken from: (a) toddler's pool—sampling 1; (b) toddler's pool—sampling 2.

Higher contents of organic pollutants were noted in the samples of washings collected from the swimming pool installation The TC concentration was in the range from 17.41 to 6.99 mgC/L (for sampling 1) and from 15.54 to 4.46 mgC/L (for sampling 2). However, the content of DOC for the samples of raw washings in samplings 1 and 2 was 9.22 ± 0.26 mgC/L and 7.82 ± 0.12 mgC/L, respectively. Similarly, as was the case in the samples of the washings from the toddler's pool installation there was a clear decrease in the TOC concentration in the successively separated fractions (Figure 3). The TOC concentration ranged from 10.99 to 1.00 mgC/L (Figure 3a) and from 8.15 to 0.93 mg/L (Figure 3b).

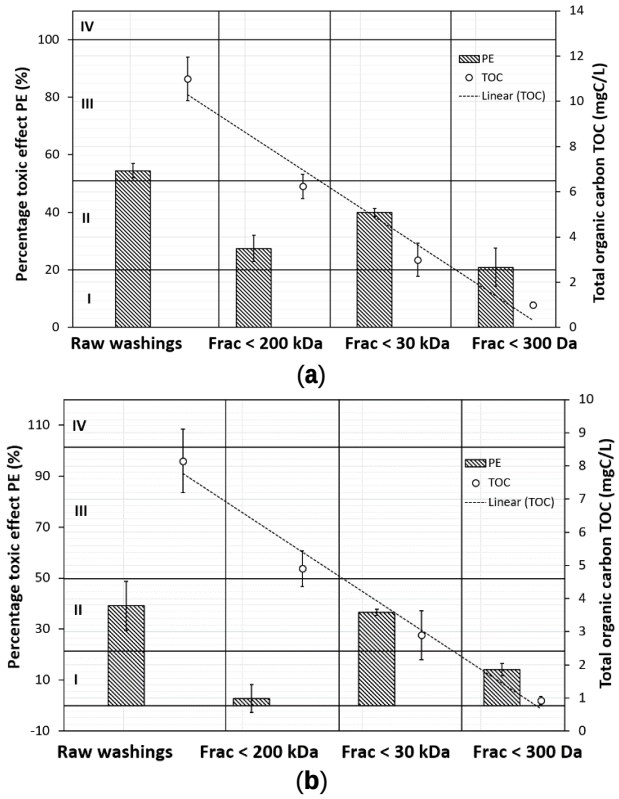

Figure 3. Values of TOC and PE in raw washings and separated fractions, samples were taken from: (a) swimming pool—sampling 1; (b) swimming pool—sampling 2.

In addition, the samples of raw washings collected in the first sampling were characterized by an acute toxic hazard for test organisms (PE equal to 54.45 ± 2.48%). The PE value recorded for the second sampling was 39.09 ± 9.53% (class II: small acute threat). The percentage effect values were lower in the separated fractions, but again, the highest value was observed for the <30 kDa fraction, PE for the 1 and 2 samplings equal to 39.92 ± 1.37% and 36.63 ± 1.23% respectively (Figure 3).

The washings from the hot tube installation were characterized by a varied content of carbon compounds depending on the sampling. In the first analysis, the TC concentration ranged from 13.84 to 4.02 mgC/L, while in the second one from 4.67 to 2.21 mgC/L. In addition, DOC values of 5.94 ± 0.21 mgC/L and 1.57 ± 0.09 mgC/L were recorded for sampling 1 and 2, respectively.

The concentration of TOC in the samples of the washings from the first sampling was in the range of 7.27 to 0.97 mgC/L. In turn, in the successively collected washings, it ranged from 2.55 to 0.80 mgC/L (Figure 4). Most of the analyzed samples were classified as having a low toxic hazard to test organisms. Again, the fraction <30 kDa was distinguished as the one with the highest percentage of toxic effect (Figure 4).

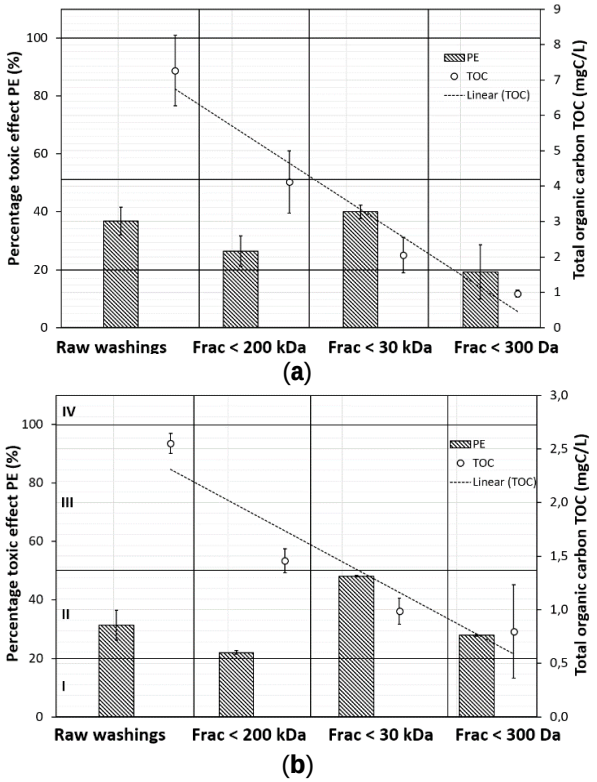

Figure 4 Values of TOC and PE in raw washings and separated fractions, samples taken from: (a) hot tub—sampling 1; (b) hot tub—sampling 2.

4. Conclusions

The use of a multistage membrane system allowed for the extended physicochemical and toxicological analysis of pool water quality. The analyzed fractions of pollutants with a molecular weight below 200 kDa, 30 kDa and 300 Da, were characterized by diversified properties:

- The presented study showed a significant share of the organic pollutants fraction with a molar weight below 300 Da in the examined washings. The quality of washings (the value of selected physicochemical parameters) varied depending on the type of pool from which the samples were taken.
- There was a clear reduction in the concentration of organic pollutants along with the subsequent processes.
- The values of TOC and DOC concentrations are commonly analyzed parameters of pool water quality. The TOC values presented in the literature show large variations, depending on a load of objects and the applied water treatment purification technology, they range from 0.70 to even 85 mgC/L [3,21–23]. It can be assumed that all values obtained in this study did not differ from the literature data (range from 0.71 to 11.00 mgC/L).
- In turn, the analysis of toxicity of separated fractions did not show the tendency presented in the studies of other authors [7]. The highest toxicity in the samples tested was observed for fractions below 30 kDa. In addition, none of the samples were classified as highly toxic to test organisms.
- There was no correlation between the concentration of TOC and the percentage of toxic effect.
- Screening toxicity tests can be a signal of the quality of environmental samples, including swimming pool water. However, analyzes of this type require the extension of additional test organisms or observations of a larger number of morphological parameters of these organisms.

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Author Contributions: Edyta Łaskawiec conceived and designed the experiments, performed the experiments and analyzed the data under the supervision of Joanna Wyczarska-Kokot and Mariusz Dudziak; Mariusz Dudziak and Mariusz Kuglarz contributed reagents materials and analysis tools; Edyta Łaskawiec wrote the paper under the supervision and review of Joanna Wyczarska-Kokot.

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References

1. Carter, R.A.A.; Joll, C.A. Occurrence and formation of disinfection by—products in the swimming pool environment: A critical review. *J Environ Sci* **2017**, *58*, pp. 19–50, DOI: 10.1016/j.jes.2017.06.013
2. Keuten, M.G.A.; Peters M.C.F.M.; Daanen H.A.M.; de Kreuk M.K.; Rietveld, L.C.; van Dijk, J.C. Quantification of continual anthropogenic pollutants released in swimming pools. *Water Res* **2014**, *53*, pp. 259–270, DOI: 10.1016/j.watres.2014.01.027
3. Chowdhury, S.; Alhooshani, K.; Karanfil, T. Disinfection by-products in swimming pool: occurrences, implications and future needs. Water Res 2014, *53*, pp. 68–109, DOI: 10.1016/j.watres.2014.01.017
4. Kanan, A.; Karanfil, T. Formation of disinfection by-products in indoor swimming pool water: The contribution from filling water natural organic matter. *Water Res* **2010**, *45(12)*, pp. 926–932, DOI:
5. Teo, T.L.L.; Coleman, H.M.; Khan, S.J. Chemical contaminants in swimming pools: Occurrence, implications and control. *Environ Int* **2015**, *76*, pp. 16–31, DOI: 10.1016/j.envint.2014.11.012
6. Farré, M.J; Day, S.; Neale, P.A.; Stalter, D.; Tang, J.Y.M.; Escher, B. Bioanalytical and chemical assessment of the disinfection by-products formation potential: Role of organic matter. *Water Res* **2013**, *47*, pp. 5409–5421, DOI: 10.1016/j.watres.2014.04.002
7. Glauner, T.; Waldmann, P.; Frimmel, F.H.; Zweiner, C. Swimming pool water—fractionation and genotoxicological characterization of organic constituents. *Water Res* **2005**, *39(18)*, pp. 4494–4502, DOI: 10.1016/j.watres.2005.09.005
8. Korkosz, A.; Janczarek, M.; Aranowski, R.; Rzechuła, J.; Hupka, J.; Efficiency of deep bed filtration in treatment of swimming pool water. *Physicochem Probl Miner Process* 2010, *44*, pp. 103–113, Available online: http://www.journalssystem.com/ppmp/Author-J.-Hupka/71085 (accessed on 27 September 2018).
9. Uhl, W.; Hartmann, C. Disinfection by—products and microbial contamination in the treatment of pool water with granular activated carbon. *Water Sci Technol* **2005**, *52(8)*, pp. 71–76, DOI: 10.2166/wst.2005.0229
10. Xiao, F.; Zhang, X.; Zhai, H.; Lo, I.M.C.; Tipoe, G.L.; Yang, M.; Pan, Y. New halogenated disinfection by-products in swimming pool water and their permeability across skin. *Environ Sci Technol* **2012**, *46(13)*, pp. 7112–7119, DOI: 10.1021/es3010656
11. Mishra, B.K.; Gupta, S.K.; Sinha, A. Human health risk analysis from disinfection by-products (DBPs) in drinking and bathing water of some Indian cities. *J Environ Health Sci Eng* **2014**, *12(73)*, pp. 1–10, DOI: 10.1186/2052–336X-12–73
12. Yeh, R.Y.L.; Farré, M.J., Stalter, D.; Tang, J.Y.M.; Molendijk, J.; Escher, B.J. Bioanalytical and chemical evaluation of disinfection by-products in swimming pool water. *Water Res* **2014**, *59*, pp. 172–184, DOI: 10.1016/j.watres.2014.04.002
13. Florentina, A.; Hautemaničrea, A.; Hartemann, P. Health effects of disinfection by-products in chlorinated swimming pools. *Int J Hyg Environ Health* **2011**, *214*, pp. 461–469, DOI: 10.1016/j.ijheh.2011.07.012
14. Du, Y.; Lu, X.T.; Wu, Q.Y.; Zhang, D.Y.; Zhou, Y.T.; Peng, L.; Hu, H.Y. Formation and control of disinfection byproducts and toxicity during reclaimed water chlorination: A review. *J Environ Sci* **2017**, *58*, pp. 51–63, DOI: 10.1016/j.jes.2017.01.013
15. Richardson, S.D.; DeMarini, D.M.; Kogevinas, M.; Fernandez, P.; Marco, E.; Lourencetti, C.; Ballesté, C.; Heederik, D.; Meliefste, K.; McKague, A.B.; Marcos, R.; Font-Ribera, L.; Grimalt, J.O.; Villanueva C.M. What's in the Pool? A comprenhensive identification of disinfection by-products and assessment of mutagenic of chlorinated and brominated swimming pool water. Environ Health Perspect 2010, 118(11), pp. 1523–1530, DOI: 10.1289/ehp.1001965
16. Manfra, L.; Canepa, S.; Piazza, V.; Faimali M. Lethal and sublethal endpoints observed for *Artemia* exposed to two reference toxicants and an ecotoxicological concern organic compound. *Ecotoxicol Environ Saf* **2016**,*123*, pp. 60–64, DOI: 10.1016/j.ecoenv.2015.08.017

17. Fantuzzi, G.; Aggazzotti, G.; Righi, E.; Predieri, G.; Castiglioni, S.; Riva, F.; Zuccato, E. Illicit drugs and pharmaceuticals in swimming pool waters. Sci Total Environ 2018, 635, pp. 956–963, DOI: 10.1016/j.scitotenv.2018.04.155
18. Wyczarska-Kokot, J. The study of possibilities for reuse of washings from swimming pool circulation systems. *Ecol Chem Eng S* **2016**, *23(3)*, pp. 447–459, DOI: 10.1515/eces-2016–0032
19. ASTM E1440–91(2012). Standard Guide for Acute Toxicity Test with the Rotifer Brachionus. ASTM International, **2012**, West Conshohocken, PA, DOI: 10.1520/E1440–91R12
20. Persoone, G.; Marsalek, B.; Blinova, I.; Törökne, A.; Zarina, D.; Manusadzianas, L.; Nalecz-Jawecki, G.; Tofan, L.; Stepanova, N.; Tothova, L.; Kolar B. A Practical and User-Friendly Toxicity Classification System with Microbiotests for Natural Waters and Wastewaters. *Environ Toxicol* **2003**, *18(6)*, pp. 395–402, DOI: 10.1002/tox.10141
21. De Laat, J.; Feng, W.; Adams Freyfer, D.; Dossier-Berne, F. Concentration levels of urea in swimming pool water and reactivity of chlorine with urea. *Water Res* **2011**, *45*, pp. 1139–1146, DOI: 10.1016/j.watres.2010.11.005
22. Keuten, M.G.A.; Schets, F.M.; Schijven, J.F.; Verberk, J.Q.J.C., van Dijk, J.C. Definition and quantification of initial anthropogenic pollutant release in swimming pools. *Water Res* **2012**, *46*, pp. 3682–3692, DOI: 10.1016/j.watres.2012.04.012
23. Lee, J.; Hab, K.T.; Zoha K.D. Characteristics of trihalomethane (THM) production and associated health risk assessment in swimming pool waters treated with different disinfection methods. Sci Total Environ 2008, 407, pp. 1990–1997, DOI: 10.1016/j.scitotenv.2008.11.021