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Physicochemical and ecotoxicological assessment of the fraction of impurities present in washings obtained in ultrafiltration and nanofiltration

Edyta Łaskawiec[a,*], Beata Fryczkowska[b], Joanna Wyczarska-Kokot[a], Mariusz Dudziak[a]

[a]*Faculty of Environmental Engineering and Energy, Department of Water and Wastewater Engineering, Silesian University of Technology, Konarskiego 18, 44-100 Gliwice, Poland, emails: edyta.laskawiec@polsl.pl/edyta.laskawiec@gmail.com (E. Łaskawiec), joanna.wyczarska-kokot@polsl.pl (J. Wyczarska-Kokot), mariusz.dudziak@polsl.pl (M. Dudziak)*
[b]*Faculty of Materials, Civil and Environmental Engineering, Institute of Textile and Polymer Materials Engineering, University of Bielsko-Biala, Willowa 2, 43-309 Bielsko-Biała, Poland, email: bfryczkowska@ath.bielsko.pl*

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ABSTRACT

The washings remaining after rinsing the pressure filters in swimming pool facilities constitute a stream representing the full array of impurities found in these waters. To separate individual fractions of these impurities, pressure membrane processes, ultra-, and nanofiltration have been used. The washings from water circuits in pools of different intended use and with various impurities were analyzed. Six fractions were obtained, with an apparent molar mass of: >200; <200; 200–30; <30 kDa; 30 kDa–300 Da; <300 Da. The quality of each fraction was evaluated in terms of physicochemical characteristics – concentration of total organic carbon (TOC), absorbable organic halogens (AOX) – and ecotoxicological characteristics (Microtox®, *Artemia salina*). The distribution of the impurities in individual fractions varied. The highest concentrations of impurities were observed in the washings from the swimming pool, in the >200 kDa fraction, 7.87, and 2.85 mg Cl/L. However, in the fraction below 300 Da, TOC and AOX concentrations reached 0.93 and 0.47 mg Cl/L, respectively. It should be noted that all analyzed samples of impurity fractions were characterized by low/nontoxicity. There was no correlation between selected physicochemical parameters, or the concentration of TOC and AOX, and the toxicity level.

Keywords: Membrane fractionation; Pool water; Washings; Apparent molar mass; Microtox; Total organic carbon

1. Introduction

Physicochemical and microbiological analysis of pool water, currently performed in the pool facilities, is necessary to control water quality. However, it does not provide complete information about other pollutants present in this environment, including disinfection by-products (DBPs) and their precursors [1,2]. Factors conducive to the formation of DBPs include the pH of treated water, turbidity (or suspended solids), temperature, concentration of natural, and anthropogenic organic matter (determined as organic carbon concentration), bromine ion concentration, and the type of disinfectant, its concentration and its contact time with water [1,3–7].

Several of these factors are analyzed indirectly by measuring physicochemical parameters. So far, research on pool water quality has focused on trihalomethanes (THMs), but compounds such as cyanide halides, halogen acetic acids (HAAs), and haloacetonitriles are also increasingly important and need to be measured [8–10].

In addition to natural organic matter, tap water supplying pool circuits contains chlorides, bromates, and DBPs, including chloramines and bromamines [11]. Therefore, one of the possibilities to reduce the amount of pollution

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* Corresponding author.

in pool waters is to use water sources present in the facility, for example, deep wells [2]. However, the main factor contributing to the deterioration of water quality in the pool basin and circulation is anthropogenic pollution, which is introduced directly into the basin. DBPs are formed by the introduction of organic matter by bathers and the continuous process of water chlorination and UV irradiation [2,12,13]. Depending on the sources, it is estimated that one bather releases 25–77 mL of urine and 200–1,000 mL of sweat, which supply the pool water with numerous organic compounds [6,14].

The concentration and composition of DBPs precursors related to human body secretions strongly depend on the number of people using the pool basin (this value is usually given as the number of people per hour or per square meter), their hygiene habits, and the purpose of using the pool (swimming, children, recreational, hot tub, and others) [2]. Pool waters have been confirmed to contain not only urea or ammonia, but also uric acid, creatinine, creatine, lactic acid, citric acid, hippuric acid, uracil, ornithine, chlorides, sulfates, K^+, Na^+, Ca^{2+}, Mg^{2+}, Zn^{2+}, and amino acids – histidine, glycine, cysteine, asparagine, lysine, arginine, and guanine [2,15–17]. Furthermore, the excreted urine contains active ingredients and metabolized products of analgesics, antibiotics, and cosmetics compounds which also react with disinfectants [16,18–22].

More than 600 DBPs have already been identified in pool waters [23,24]. These compounds include various chemical species, such as THMs, haloacetates, HAAs, halonitriles, halogenobenzoquinones, chloroacetonitriles, and halogenamides [2,24]. Therefore, it is necessary to extend the physicochemical analysis with additional parameters that will also allow to assess the potential harmfulness of DBPs. Furthermore, while determining the quality of pool water, it is also essential to analyze the correlation of selected parameters.

In addition to turbidity, the additional parameters that describe the relationship between water quality and the presence of DBPs include the concentration of dissolved and total organic carbon (TOC), total nitrogen, organic nitrogen (considering the importance of urea-containing groups); the total content of inorganic salts (TDS) and the value of UV absorbance measured at 254 nm (UVA_{254}) [25,26]. It should also be remembered that the last parameter is not entirely selective to impurities from the group of DBPs. However, despite the limitation, the analysis based on UVA_{254} has been repeatedly used to control the quality of disinfected water. The UV absorbance value is a measure of aromaticity and can be an indicator of the potential for THMs and HAA formation in pool water, but it is not a direct determinant of the concentration of DBPs [27].

The concentration of carbon compounds in pool water is directly related to the pool load of the basin and the formation of DBPs, especially from precursors associated with secretions of the human body. Therefore, the concentration of TOC shows a strong correlation with the concentration of DBPs in pool water [25,26,28]. The concentration of THMs, heterocyclic aromatic amines, and HAAs correlate with the number of bathers in the pool and the concentration of TOC [12,13,29]. The concentration of TOC also shows a strong correlation with the concentration of nitrogen compounds in the pool water and turbidity [30]. To assess the content of DBPs, it is essential to determine the concentration of dissolved organic carbon, which can be minimized in the circulation only by diluting the pool water with a dose of fresh tap water [26,31].

Routes of exposure to DBPs may vary depending on the nature of the chemical [6]. For example, volatile THMs enter the human body through the respiratory tract and skin, and their presence has been confirmed in both the alveoli and blood plasma [32–34]. In contrast, trichloramines and tribromoamines migrate deep into the body through the skin [6,35]. Direct consumption (also in the form of aerosols) and migration into the bloodstream is a characteristic of some chemical compounds, such as HAAs [6,33].

The exposure assessment of compounds present in pool water should include many variables, including the number of people in the basin and its cubage, the size of the swimming pool hall, water temperature, and the efficiency of the air circulation process [2,23].

Although many of the DBPs in the tested pool water samples are present in concentrations below 1 mg/dm^3, their presence is still harmful to people using the swimming pool [36]. Chloroform contributes to the destruction of the barrier function of the epidermis in people with sensitive and/or atopic skin [37]. Moreover, eye irritation or irritating smell often smelled during bathing is the effect of chloramines which, contrary to popular belief, are not the most harmful DBPs. The most dangerous effects of DBPs are not noticed in many years of regular bathing. Asthma, bladder cancer, and atopic dermatitis are being increasingly recognized as risks to the health of pool users and facility employees [2,4,38,39]. It has also been confirmed that microcontaminants of various enzymes, produced as DBPs, lead to the generation of oxidative stress in the cells of living organisms [40]. Research in the field of pool water quality assessment using toxicological tests have revealed that some of these compounds have genotoxic, cytotoxic, or mutagenic properties [12,36,40]. In this regard, contacting with haloacetonitriles poses a higher risk than contact with THMs [4]. Furthermore, both organic and inorganic UV filter components have been reported to possess estrogenic and androgenic properties [18].

Physicochemical analysis of washings, which are obtained in the backwashing process of porous filter beds, may play an essential role in the comprehensive assessment of pool water quality. The washings can be treated as a stream reflecting the full range of pollutant fractions present in the pool water. The washings are characterized by a large number of suspension and coagulant residues used during treatment [41]. The organic matter in the washings is primarily concentrated around particles larger than 45 μm [41]. A large proportion of the 30 μm fraction, as well as nanoparticles of approximately 955 nm in size, were also noted [42]. The presence of DBPs, high concentration of free chlorine, and pathogenic microorganisms, such as *Giardia lamblia* and *Cryptosporidium*, have also been confirmed [42–48]. Less frequent are instances of significant exceedance in terms of chemical oxygen demand (COD) and total phosphorus concentration [48,49].

One of the possibilities of separating such a diverse group of impurities is to perform multistage membrane filtration (membrane fractionation). On the basis of the knowledge about the size of particles present in washings and swimming pool water, pressure processes such as microfiltration, ultrafiltration, and nanofiltration can be used for separating impurities [50]. The separated impurity fractions in the form of permeate and retentate can be characterized using molecular weight cut-off (MWCO) membranes or by assigning apparent molar mass to describe the fractions of pollutants [51,52].

High genotoxicity is associated with a low molar mass of DBPs [53–55]. Most DBPs have a molar mass below 1,000 g/mol [12,56]. For example, the fraction above 1,000 g/mol may be only 14%, while the fraction below 200 g/mol is approximately 30% [12]. However, although lower molar mass DBPs often show higher cytotoxicity, the latest reports also reveal the harmfulness of unregulated high molar mass pollutants [2,56].

Numerous specialized toxicological analyses have investigated the effects of DBPs. The use of simple screening tests should also be considered as they can reduce costs and do not require specialized staff to perform them [49,57–59]. An assessment of pool water and washings quality, including the use of ecotoxicology tools, could be such an alternative.

Ecotoxicology can be approached comprehensively. The effect of the level of contamination on indicator organisms is assessed according to the overall response to a diverse range of toxic or potentially toxic substances in terms of chemical nature and concentration. The results of these analyses may be inferred in terms of risks posed by the contact of the toxicant with the environment [60].

The group of organisms used in ecotoxicological analyses includes bacteria, plants and animals. The classifications of ecotoxicological quality (or ecotoxicity classification) consider toxic effects in terms of toxicity units (TU) or percentages by referring to reference samples (without the analyzed toxicant) and the level of significance of the results. Most of these types of classification relate their values to the results obtained in more than one biotest using different organisms [60–63].

The first of the commercial biotests, which was based on miniaturization, speed, and simplicity of performance was the luminescence inhibition test of lyophilized bacteria *Aliivibrio fischeri* [64]. A decrease in the amount of light emitted (inhibition of bioluminescence) implies a slowdown in metabolic processes and is an indicator of the relative toxicity of the test sample. Compounds present in the samples can also stimulate metabolism, thereby resulting in increased light output [62,65,66]. Most of the tested toxicants show similar sensitivity towards higher organisms, including crustaceans and fish [67,68].

Modern ecotoxicological tools offer many possibilities for extensive analyses, including determining the relationship in terms of the sensitivity of different organisms to the same toxic substance.

The present study aimed to perform a comprehensive analysis of the quality of washings samples from multi-use swimming pool circuits. A detailed assessment of the quality of the washings was determined by means of membrane fractionation with ultrafiltration and nanofiltration processes. It allowed to assess of the physicochemical and ecotoxicological quality of raw washings and separated fractions of impurities.

2. Research materials and experimental methods

2.1. Research objects

The study investigated washings obtained after washing the filter beds, as well as permeates, obtained from membrane fractionation processes, and concentrated retentates. Selected parameters of pool water treatment circuits are presented in Table 1. Washings from the circuits for a swimming lessons pool (SWP), a hot tub (HT), and a common toddler pool and hot tub (TP + HT) were analyzed. Each circuit was located in a different facility. All pressure filters had sand or zeolite multilayer beds with a hydroanthracite layer.

In all circuits, the water was treated using the following processes: contact coagulation – pressure filtration – pH correction (sulfuric acid) – disinfection (sodium hypochlorite, produced in the membrane electrolysis process).

The washings were collected immediately after the facilities were closed. The beds were rinsed in plastic canisters without leaving an air gap. The samples were analyzed in the morning for selected physicochemical parameters described in section 2.2 (physicochemical analysis).

2.2. Physicochemical analysis

An analysis of selected physicochemical parameters of raw and fractionated washings was performed. The pH and redox potential were determined by the potentiometric method, while the conductivity was determined by conductometry (multiparameter meter inoLab® 740/WTW, measuring and analytical technical equipment, (Wroclaw, Poland)). The turbidity of the samples was determined using a portable device turbidimeter TN-100/EUTECH Instruments (Waltham, USA). The absorbance of the filtered samples was determined using a single beam spectrophotometer (UV VIS Cecil 1000, Analytik Jena AG, Jena, Germany). The free and total chlorine and potassium concentrations were determined colorimetrically using cuvette

Table 1
Characteristics of pool circuits and sources of washings for membrane fractionation

Pool	Symbol	Pool capacity (m^3)	Number of filters	Filter diameter (mm)	Filter bed type
Swimming	SWP	121.10	2	1,250	Sand multilayer with hydroanthracite
Hot tub	HT	3.70	1	2,000	
Toddler + hot tub	TP+HT	24.90 + 4.00	1	1,800	Zeolite multilayer with hydroanthracite

tests. Nitrates, ammonium nitrogen, total nitrogen, sulfur, COD, cyanuric acid, phenol index, aluminum, and adsorbable organic halogens (AOX) were determined spectrophotometrically (UV-VIS Spectroquant® Pharo 300, Merck, Dramstadt, Germany). The concentration of TOC was determined by catalytic combustion (TOC-L series, Shimadzu, Kyoto, Japan).

2.3. Ecotoxicological assessment

Toxicity analysis was performed using the screening test procedure of the MicrotoxOmni System in the Microtox® Model 500 (Tigret) analyzer, which acts as both an incubator and a photometer. Percent inhibition relative to the untreated toxicant control in pool water samples and/or washings was measured after 5 and 15 min of exposure time. The effect of toxicity was defined as the percentage inhibition of bioluminescence of *A. fischeri* (*E*, %). The results of toxic effect values were used for an exposure time of 15 min.

The ecotoxicological tests of the samples were repeated every time and in triplicate.

Due to the high sensitivity of the method and significant values of the standard deviation, it was decided to carry out the test using the second indicator organism.

The toxicity assessment of the tested pool water samples was also based on the mortality test for the crustacean larvae *A. salina*. The organisms were obtained from a test culture conducted according to the methods based on the experiments presented in the literature [69,70]. The studies were performed at the second/third stage of larvae development, which is considered to be most sensitive to toxicants [70]. The analyzed samples were added to the test wells, and 10 larvae were then introduced into the wells. The number of dead and/or immobilized organisms was determined after 24 and 48 h of incubation. The toxicity effect *E* was calculated for each sample of the tested pool water and the control sample constituting a brine solution for crustacean farming. The results of toxic effect values were used for an exposure time of 48 h. All biotests were performed after assessing the chlorine concentration in the samples (total chlorine ≤ 0.1 mg Cl_2/L). The ecotoxicological tests of the samples were repeated every time and in triplicate.

Toxicity effect (*E*, %) for the biotests was determined from the following relationship: $E = (100 \cdot (E_K - E_T))/E_K$, where E_K is the observed effect for the control sample and E_T is the observed effect for the test sample (raw washings, permeate, and retentate).

The results were related to the duration of observation in a given test. A system used to classify toxicity was based on the amount of the observed effect of toxicity (*E*) induced in the indicator organism [62,63]. The toxicity classification used in the interpretation of the results is one of the standard ones. It enables assigning the obtained results to a specific class proving a toxic effect or no toxicity. Toxicity classes with the corresponding percentages are given in Table 2.

2.4. Determination of the apparent molar mass by membrane fractionation

As part of the research, it was assumed that it is possible to use membranes with different distribution properties (MWCO) to separate selected fractions of impurities present in raw washings. Several membrane filtrations were performed in a multistage (dead-end) system. The diagram of the continuous processes is shown in Fig. 1. Filtration was performed in a 380 mL filtration cell equipped with a magnetic stirrer at a constant temperature of 20°C; the active filtration surface of the membrane was 38.5 cm^2. The membrane filtration tests were performed in the following sequence: membrane conditioning with deionized water – washings filtration – membrane rinsing (in the direction of filtration) and, at every stage: UF I – UF II – NF. Transmembrane pressure was 0.2 and 1.0 MPa in ultrafiltration and nanofiltration processes, respectively (Fig. 1).

Selected ultrafiltration and nanofiltration membranes with different separation capacities were used to separate the impurity fraction. Table 3 presents the characteristics of the membranes. Separated fractions of impurities with different apparent molar masses were subjected to physicochemical and ecotoxicological assessment.

2.5. Membrane imaging following membrane fractionation processes

The stability of membrane materials and the degree of their contamination were assessed by imaging using the scanning electron microscopy (SEM), t_j. JSM 5500LV (JEOL, Japan) at the Institute of Textile and Polymer Materials Engineering of the University of Bielsko-Biała. This stage was to assess the share of negative phenomena during the fractionation of pool water, which could contribute to distorting the results of the analyses.

2.6. Additional tools for analysis of results

Analysis of physicochemical results was based on the data analysis package in Microsoft Excel. Average values (*M*), standard deviation (SD), and correlation coefficient (*r*) were calculated.

3. Results and discussion

3.1. Physicochemical quality of the fractionated washings

Pool water quality is constantly monitored for chemical and organic impurities. The basic physicochemical parameters of the pool water are measured several times a day or are monitored in a continuous manner. However, raw washings are usually treated as wastewater and introduced into the sewage system despite the fact that the water quality of raw washings generally reflects the water

Table 2
Toxicity classification system [63,64]

E, %	Toxicity class
<25	Non-toxic
25–50	Low-toxic
50.1–75	Toxic
75.1–100	High-toxic

quality in the entire system [32,47,49]. According to our results, the raw washings collected from the selected pool water treatment systems were characterized by a similar water quality (Table 4). The pH of the raw washings ranged between 6.82 and 7.36, and its lowest level was recorded for the samples collected from the swimming pool system (Table 4). It is noteworthy that pH of the pool water is an important indicator of the water quality as it shows the use of disinfectants and the formation of DBPs. It is assumed that high usage of disinfectants is a result of incorrectly conducted filtration process, which often manifests itself into high pH of the pool water (above 7.8). Thus, it is possible to reduce the usage of DBPs with an efficient filtration of the pool water (optimum pH should be in the range of 7.2–7.4), when the coagulation is conducted on a continuous basis [1,71]. The pH of the pool water circulating in the system undergoes fluctuations due to the changes in the temperature, presence of contaminants, or its transport. Furthermore, pH of the pool water in turn affects the efficiency of the coagulation process and the rate and efficiency of the disinfection process [1].

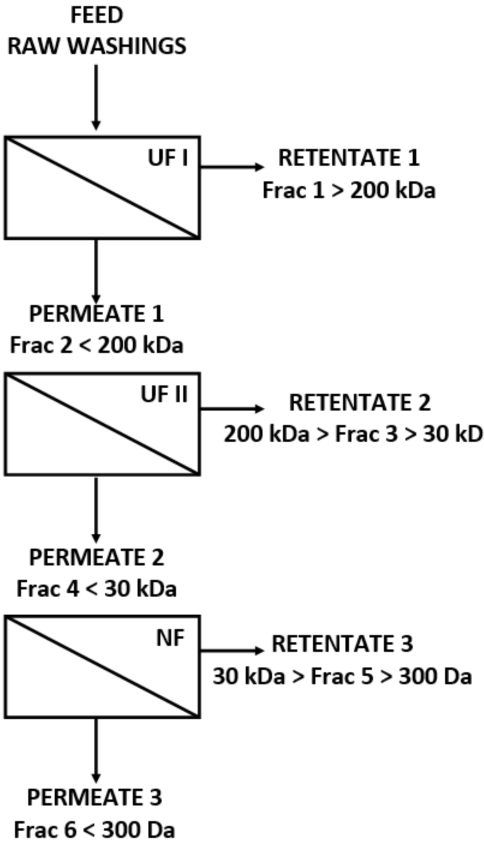

Fig. 1. Membrane fractionation process for raw washings [72].

In this study, the specific conductivity of the raw washings ranged from 868.72 μS/cm (common TP + HT circulation, multi-layer filter with a zeolite layer) to 1,102.00 μS/cm (SWP circulation and multi-layer sand filter). The specific conductivity value provides information regarding the total content of inorganic salts in the raw washings, including the proportion of contaminants that are of anthropogenic origin. The redox potential of the raw washings ranged between 286 and 652 mV (Table 4), and it is recommended that this value should be close to 750 mV for pool water [72]. The control of this parameter is extremely important from the point of view of the rate of destruction of pathogenic microorganisms. It is assumed that the risk of bacteriological contamination of water decreases with the increase of the redox potential from 770 to 800 mV. Moreover, a large amount of disinfectant and a small amount of contamination translate into a high value of the redox potential [47]. It is recommended that the redox potential should be close to 800 mV [47].

Furthermore, the following factors facilitate the formation of DBPs due to their relationship with contaminants of anthropogenic origin: DOC and TOC, respectively, total nitrogen, organic nitrogen (taking into account the importance of the units present in urea), potassium, combined chlorine, and the absorbance value at 254 nm (UV_{254}) [1,3–7,25,26]. However, it should be noted that the absorbance value of the raw washings does not entirely reflect the level of DBPs present in the water. Generally, disinfected water quality control is assumed based on the absorbance value at 254 nm. The absorbance value at this wavelength is a measure of aromaticity and it may be the indicator of the potential of formation of THMs and HAAs in pool water. However, it is not a direct determinant of the concentration of DBPs [69].

During the disinfection, some chlorine is used to destroy the bacteria, some to oxidize the organic compounds, some remain unbound, and the rest form chloramines (analyzed in terms of the bound chlorine parameter) by combining with ammonium nitrogen. Maintaining the concentration of bound chlorine at a low level is a big problem for many objects under analysis [8].

One of the indicators of pollution associated with physical activity in swimming pool water may be the measurement of potassium concentration. It is estimated that as much as 90% of potassium in the human body is excreted in the urine (the average value is 100 mmol/d) [73].

Table 3
Membrane characteristics according to the manufacturer's data

Process	Membrane symbol	Manufacturer	Membrane material	MWCO, Da
UF	(*V*5) YMV53001	Synder filtration™	Polyvinylidene fluoride (PVDF)	200,000
	(*V*3) YMV33001	Synder filtration™	PVDF	30,000
NF	(NF90) YMNF903001	DOW FILMTEC™	Polyamide-TFC*	200–300

*TFC: thin film composite.

Table 4
Physicochemical data of raw washings

Parameter, unit	Pool water cycle		
	SWP	HT	TP + HT
pH, –	6.82	7.36	7.20
Conductivity, µS/cm	1,102.00	966.80	868.72
Redox potential, mV	286	652	429
Turbidity, NTU	37.00	21.00	11.00
Absorbance UVA_{254} (filtered samples), m^{-1}	16.90	14.20	8.20
Free chlorine, mg Cl_2/L	0.42	0.36	0.28
Total chlorine, mg Cl_2/L	0.96	0.85	0.69
Potassium, mg K/L	4.80	3.80	4.10
Nitrates, mg NO_3^-/L	3.50	3.10	2.80
Ammonium nitrogen, mg $N–NH_4$/L	0.20	0.10	0.20
Total nitrogen, mg N/L	8.20	7.50	8.00
Sulfur, mg SO_4^{2-}/L	96	92	98
COD, mg O_2L	25	>15	>15
Cyanuric acid, mg $C_3H_3N_3O_3$/L	4.10	3.50	4.00
Phenol index, mg C_6H_6O/L	0.48	0.32	0.42
Aluminum, mg Al/L	0.70	0.64	0.71
AOX, mg Cl/L	2.92	2.84	2.17
TOC, mg C/L	8.15	2.55	5.95

SWP: swimming pool water; HT: hot tub; TP: toddler pool; NTU: nephelometric turbidity units; COD: chemical oxygen demand; AOX: adsorbable organic halogens; TOC: total organic carbon.

The concentration of potassium ions in the collected samples ranged from 3.80 to 4.80 mg K/L.

A relatively low concentration of nitrogen compounds was also noted in the tested samples [48].

Among the parameters specified in Table 4, one needs to pay attention to the TOC content, which ranges between 2.55 mg C/L (HT) and 8.15 mg C/L (SWP; Table 5). The values obtained are relatively low, considering the concentrations recorded in the source data (3–125 mg C/dm^3) [2,74]. Furthermore, the level of AOX may constitute an indirect assessment of low-molecular compounds in the sample, which provides information about the genotoxic potential of the analyzed pool water [75].

According to the results, after the coagulation process was conducted on the raw washings, there was a great amount of residue left behind. Turbidity of the raw washings ranged from 11 NTU (TP + HT) to 37 NTU (SWP), which was mainly caused by the presence of disintegrated flocculent particles stemming from the coagulation process. In addition, the level of aluminum that remained after the coagulation process was in the range of 0.64–0.71 mg Al/L (Table 4).

The quality of raw washings depends on a range of factors, such as length of the filtration cycle, type and number of filters, rinsing method, quality of the supplied water, the technology used, and hydraulic conditions of the pool [47]. Moreover, their quality varies during rinsing, with the highest amount of contaminants being rinsed at the beginning of the process [47,76]. Among the analyzed washings, the lowest quality was recorded for the samples collected from the swimming pool. The values of the physicochemical parameters point to the contribution of the contaminants of anthropogenic origin and coagulation products in the washings (high turbidity and residual aluminum). The presence of cyanuric acid in the samples is also associated with the use of coagulants in the swimming pool facilities [77,78].

3.2. Physicochemical characteristics of the selected contaminant fractions in the washings

For each contaminant, 12 filtration cycles were conducted. Figs. 2a and b show values of the mean concentration of TOC and the mean total concentration of AOX.

The TOC content in the fraction containing compounds with high apparent molecular weight (>200 kDa) differed depending on the origin of the washing; the highest and the lowest levels of TOC were recorded for SWP and HT samples (7.87 ± 0.79 and 2.25 ± 0.17 mg C/L, respectively) (Fig. 2a). The level of AOX in the fraction containing compounds with molecular weight >200 kDa was similar in all the tested samples (2.85 ± 0.17, 2.51 ± 0.15, and 2.23 ± 0.10 mg Cl/L for SWP, HT, and TP + HT, respectively). The first stage of ultrafiltration (UF), resulted in a concentrated retentate (a fraction with apparent molecular weight >200 kDa) with colloids, macromolecular compounds, and post-coagulation sediments [79,80]. However, the treated permeate that was separated (a fraction with apparent molecular weight <200 kDa) still contained various amounts of organic and inorganic contaminants. The turbidity of the fraction containing compounds with molecular weight >200 kDa was 0.76, 0.34, and 0.57 NTU respectively for SWP, HT, and TP + HT systems. UV absorbance at 254 nm for this fraction ranged between 2.16 (HT) and 0.41 m^{-1} (TP + HT). The fraction containing compounds with molecular weight <200 kDa was characterized by a lower content of TOC and AOX. The content of TOC in the fraction containing compounds with apparent molecular weight <200 kDa for SWP, HT, and TP + HT was 4.90 ± 0.58, 1.46 ± 0.11, and 4.18 ± 0.09 mg C/L, respectively (Fig. 2a). Furthermore, in the fraction containing compounds with molecular weight <200 kDa lower levels of AOX were obtained: 1.92 ± 0.20, 1.85 ± 0.08, and 1.82 mg Cl/L, respectively, for the SWP, HT, TP + HP systems (Fig. 2b).

In the second stage of UF, fractions containing compounds with a molecular weight ranging from 200 to 30 and <30 kDa were obtained (Fig. 2). It should be noted that the TOC content in the fractions containing compounds with 200–30 kDa molecular weight for the samples collected from SWP and TP + HT systems was 6.24 ± 0.20 and 5.34 ± 0.76 mg C/L, respectively (Fig. 2a). The TOC content in fractions containing compounds with <30 kDa molecular weight was 2.88 ± 0.35, 0.99 ± 0.12, and 1.65 ± 0.57 mg C/L respectively for samples collected from SWP, HT, and TP + HT systems (Fig. 2). In the fraction containing compounds with 30 kDa–300 Da apparent molecular weight, an increase in the level of TOC was observed for all the tested samples. It should be emphasized that the concentration of contaminants in the retentate samples (fractions with >200, 200–30 kDa, and 30 kDa–300 Da molecular weight) was due to the level of TOC, and was not as pronounced for AOX (Fig. 2b). The total concentration of AOX in other fractions was gradually reduced (with the exception of the fraction containing 30 kDa–300 Da molecular weight for the SWP sample).

3.3. Correlation between various physicochemical parameters

The level of TOC in the pool water and raw washings is directly linked to the individual load of the pool and the formation of DBPs, particularly from the precursors associated with human body secretions. Thus, the TOC content exhibits strong correlation with their concentration in pool water [25,26,28]. In addition, the concentration of trihalogenomethanes, heterocyclic aromatic amines, and haloacetic acids correlate with the number of persons in the pool and with the TOC concentration [12,13,29].

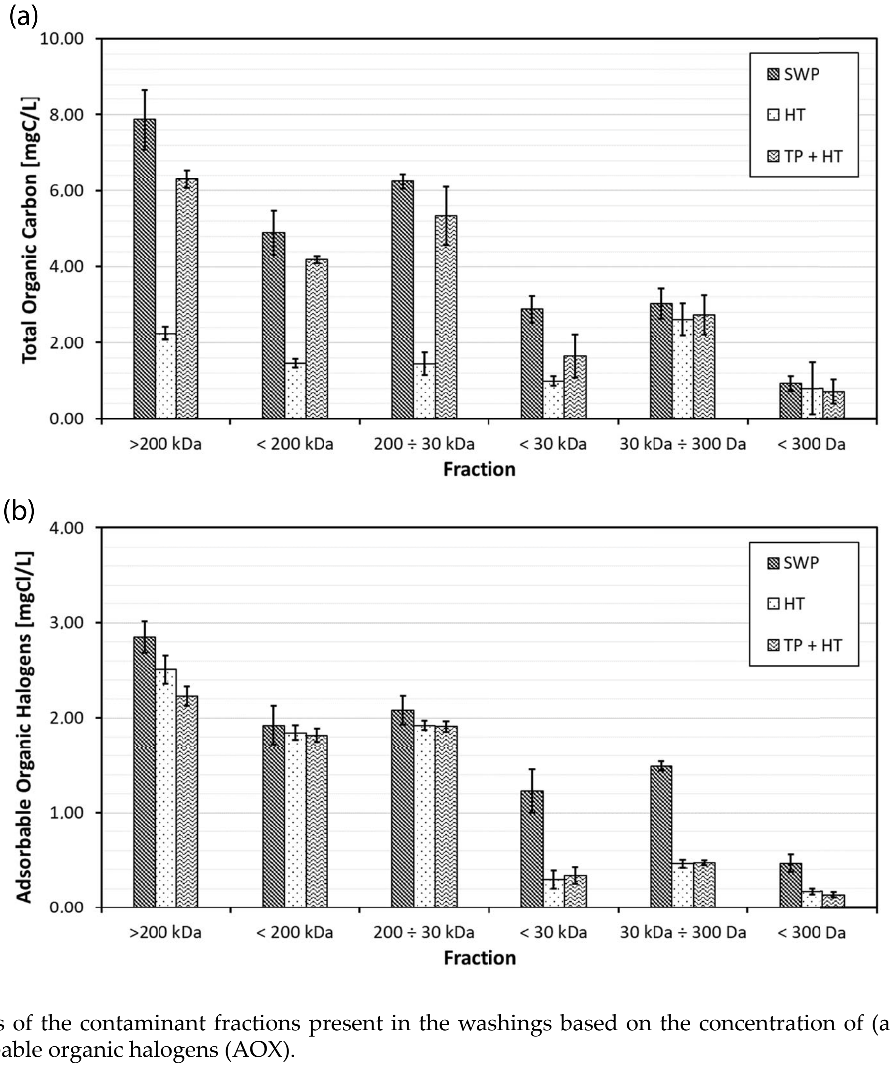

Fig. 2. Characteristics of the contaminant fractions present in the washings based on the concentration of (a) total organic carbon (TOC) and (b) adsorbable organic halogens (AOX).

Furthermore, the TOC content showed strong correlation with the level of nitrogen compounds and turbidity of the pool water [30]. For the purposes of assessing the amount of DBPs, it is important to assess the level of DOC, which can only be minimized by diluting the pool water with fresh municipal water [26,31].

In this study, the correlation between the following physicochemical parameters from the viewpoint of washings quality was analyzed: between TOC and turbidity, and between TOC and absorbance at 254 nm (where the absorbance values were higher than zero). The level of correlation between these parameters varied depending on the analyzed fraction and the type of washings. Higher correlation was obtained for fractions containing compounds with >200 kDa molecular weight (especially for the washings from the swimming pool system) (Figs. 3a–f). However, no correlation between TOC and absorbance value and turbidity were found for fractions <30 kDa and 30 kDa–300 Da. For fractions below 30 kDa, the value of ultraviolet absorbance in most of the analyzed samples was 0.00 m^{-1}. It was possible to determine the value of the correlation coefficient for values greater than naught. The TOC-turbidity correlation coefficient for HT was $r = -0.26$. TOC-UV254 correlation coefficients for SWP, HT, and TP + HT samples (fraction 30 kDa–300 Da) were, respectively, 0.04, 0.21, and 0.14. Moreover, a weak TOC-turbidity correlation was noted for SWP and TP + HT samples, the value of the coefficient was respectively: –0.17, 0.07.

3.4. SEM imaging of membrane surfaces

Analysis of the individual fractions obtained from membrane filtration should take the structure of the utilized membrane into account. The filtration was performed

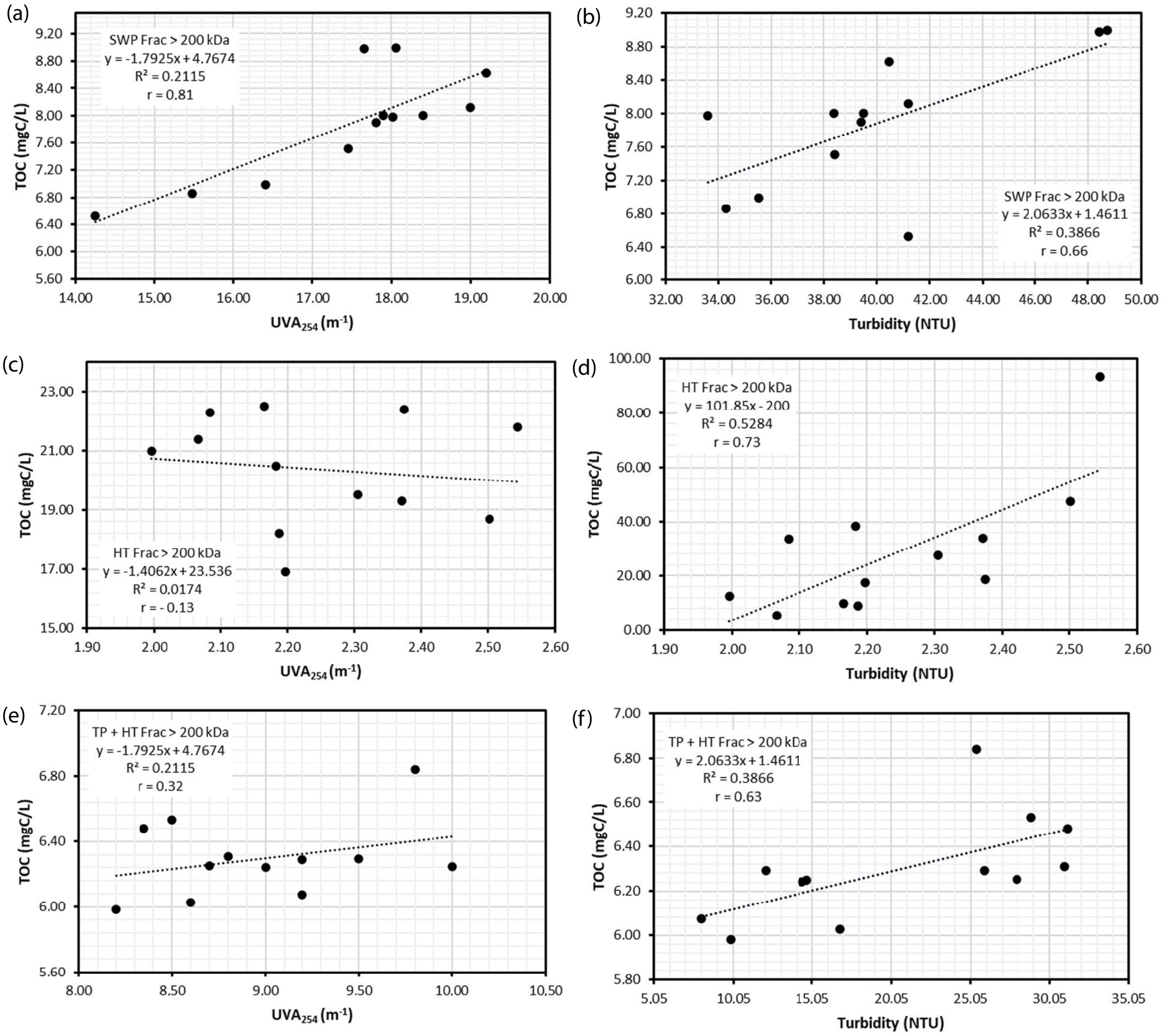

Fig. 3. Correlation of the selected physicochemical parameters in contaminant fraction with >200 kDa, for washings from the swimming pool system: (a) total organic carbon (TOC) and UVA_{254}, (b) TOC and turbidity; hot tub: (c) TOC-UVA_{254}, (d) TOC-turbidity; common system for toddler pool and hot tub: (e) TOC-UVA_{254}, (f) TOC-turbidity.

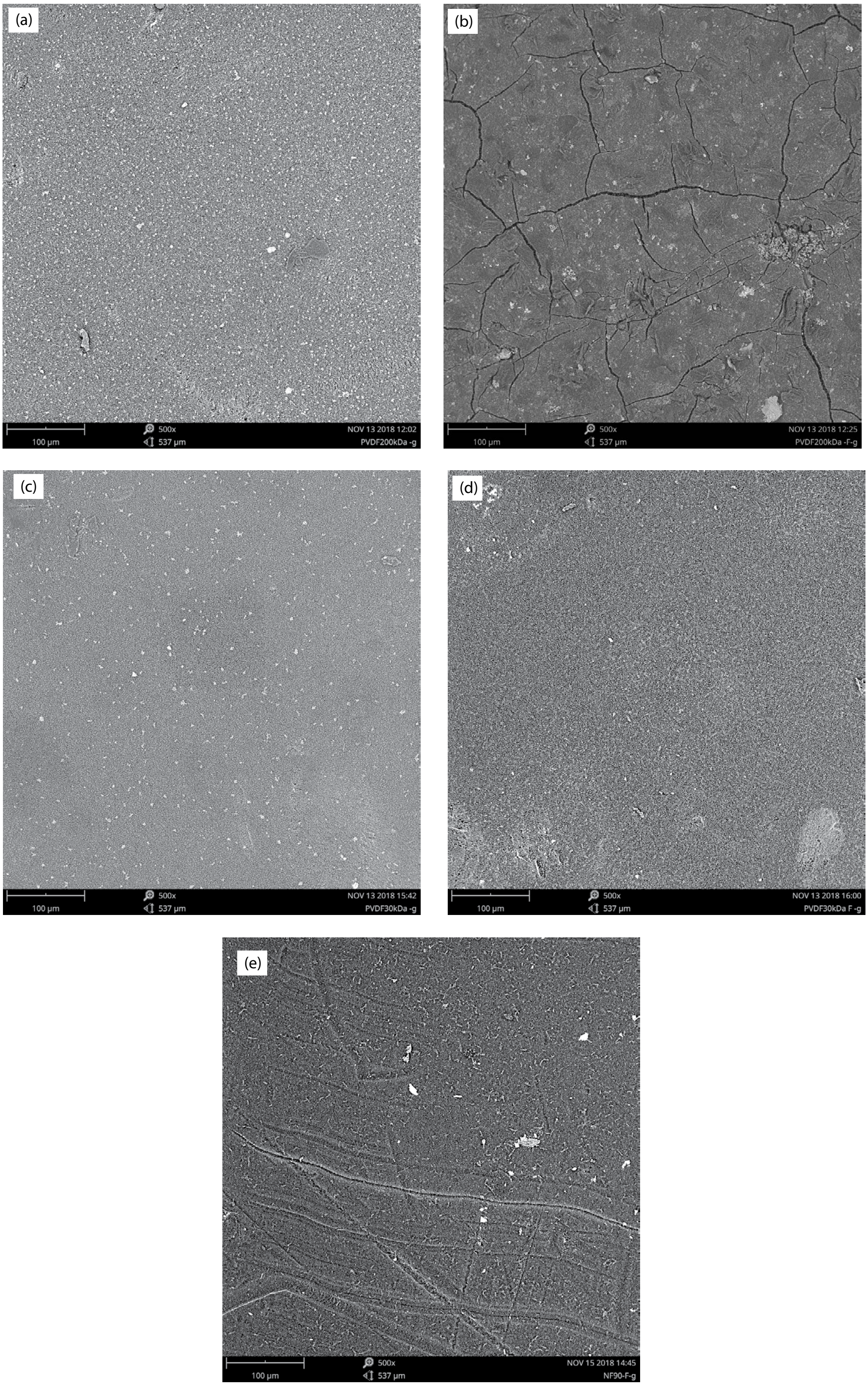

Fig. 4. Scanning electron microscopic images of ultra- and nano-filtration (UF and NF, respectively) membranes used in the process of membrane fractionation UF-I (*V*5) YMV53001 (MWCO = 200 kDa): (a) after conditioning, (b) after filtration, UF-II (*V*3) YMV33001 (MWCO = 30 kDa), (c) after conditioning, (d) after filtration; NF (NF 90) YMNF903001 (200–300 Da): (e) after conditioning, (f) after filtration.

in the dead-end flow, where the stream flows perpendicular to the membrane placed in the filtration cell. Despite the continuous washing and the periodic cleaning and rinsing of the membrane, diverse contaminants, such as solids easily accumulating onto microcontaminants, are present in the water; this blocks the pores of the membrane, causing a filter cake [81]. Both of these are easily removable. Furthermore, the partial permanent blockage of the pores decreases the diameter of the membrane pores. The most difficult problem from the viewpoint of this study is not the decrease in transport capacities of the membranes during filtration, but the increased separation capacities with the subsequent filtration cycles (therefore the authors decided that the emphasis on the mean, and dismissal of the extreme, values during the statistical elaboration of the results was a correct decision). As a result of dead-end filtration, the composition of washings is changed to some extent in the process. The feed is gradually concentrated into retentate, and an increased value of some physicochemical parameters is observed, including turbidity and TOC, depending on the assumed recovery level. In this study, each filtration cycle was set to 50% recovery of the filtered liquid.

Figs. 4a–f shows photographs of membranes used in the multistage system UF-I–UF-II–NF, before the filtration process (left), and after the completion of all filtration cycles (right). The most pronounced changes were observed for the UF membranes. The accumulation of solids on the surface, as well as cracks, scratches, and local structural damage were caused by the presence of post-coagulation sediments, contaminants, and chlorine. The process of degradation of the membrane surface is particularly clearly visible for the membrane used in the first filtration stage (Fig. 4b). This membrane was exposed to the greatest number of various negative factors. However, the NF membrane, being the last fractionation stage, was in good condition and there was no clearly visible damage (Fig. 4f).

3.5. Ecotoxicological assessment of contaminant fractions in the washings

In this study, the potential ecotoxicological assessment of the raw washings and separated fractions was performed using two screening tests with similar level of sensitivity: bacterial bioluminescence inhibition test using Microtox® test and analyzing the survival rate of *Artemia salina* larvae in 48 h time [82,83]. Figs. 5a–c presents comparison of the results of the biotests with the classification of their level of toxicity (Table 3).

According to the results, the raw washings were classified as less toxic (for *A. salina*). Values of bioluminescence inhibition were 32.35% ± 8.31%, 27.82% ± 3.62%, and 28.12% ± 5.24% for SWP, HT, and TP + HT washings, respectively (Fig. 5). Furthermore, for the washings from HT and TP + HT systems, similar mortality values of *A. salina* were obtained: 30.00% ± 5.00% and 31.67% ± 2.89%, respectively. However, in the case of SWP, the mortality rate was almost two times lower than that of the bioluminescence inhibition value (Fig. 5a). An interesting phenomenon was the increase in the toxic effect of fractions containing contaminants with molecular weight ranging from 200–30 kDa to <30 kDa. The toxicity of these fractions was greater for the washings obtained from the swimming pool and hot tub systems (Figs. 5a and b). Inhibition of the bacterial bioluminescence from *A. fischeri* for the washings obtained from the swimming pool was 34.96% ± 9.63% and 35.76% ± 7.17% for fractions 200–30 kDa and <30 kDa, respectively (Fig. 5a). The toxic effect in the *A. salina* test for 200–30 kDa fraction was similar for all samples, whereas in the case of <30 kDa fraction, the %*E* value was lower (46.67% ± 5.77%).

HT samples demonstrated the highest level of toxicity for <30 kDa fractions, its toxic effect was 48.91% ± 3.94% and 58.33% ± 7.64% for Microtox® crustacean larvae survival test, respectively (Fig. 5b).

The lowest toxicity values were recorded for the samples collected from the common circulation of TP + HT. For fractions <200 kDa and <300 Da, the bioluminescence inhibition revealed negative values (−10.10% ± 11.10% and −4.92% ± 27.54%, respectively), but the high values of standard deviation should be taken into account (Fig. 5c).

The results of this study with regard to the analysis of toxicity of the separated fractions do not agree with those reported in the literature (high toxicity of the fractions containing the smallest molecular weights) [56]. The fraction containing compounds with molecular weight of <300 Da was nontoxic in all the analyzed samples. The highest toxicity was recorded for fractions containing compounds with molecular weight of 200–30 kDa and <30 kDa. None of the investigated samples could be classified as highly toxic toward test organisms. Furthermore, no correlation between the elevated concentration of TOC and high percentage of the toxic effect could be determined. Preliminary assessment of selected fractions of impurities in washings demonstrated similar trends [84]. On the other hand, the scope of research has been significantly expanded. The lowest toxicity effect was detected for the <200 kDa fraction, the highest *E*% values were identified for the <30 kDa fraction. At the same time, individual samples of washings from the circuits of the swimming pool proved to be toxic (effect over 60%) [81]. The Microtox® microtest used in the eco-toxicological assessment is based on the determination of the inhibition of the luminescence of freeze-dried bacteria, which under normal conditions use about 10% of the energy obtained from metabolism for the production of light. The presence of toxic compounds in the analyzed samples is directly proportional to the reduction of their bioluminescence ability. A species of crustacean, which also prefers salt waters, was used to compare the obtained results – *A. salina*, however, one should take into account the extended assessment time up to 48 h and the analysis of their survivability in the presence of toxic components [85,86].

4. Conclusions

- Washings from the circuits of the swimming pool, hot tub, and toddler pool + hot tub had similar properties: increased turbidity (11–37 NTU), absorbance in UVA_{254} (8.20–16.90 m^{-1}), the concentration of TOC (2.55–8.15 mg C/L), absorbable organic halogen compounds (2.17–2.92 mg Cl/L). It should be pointed out

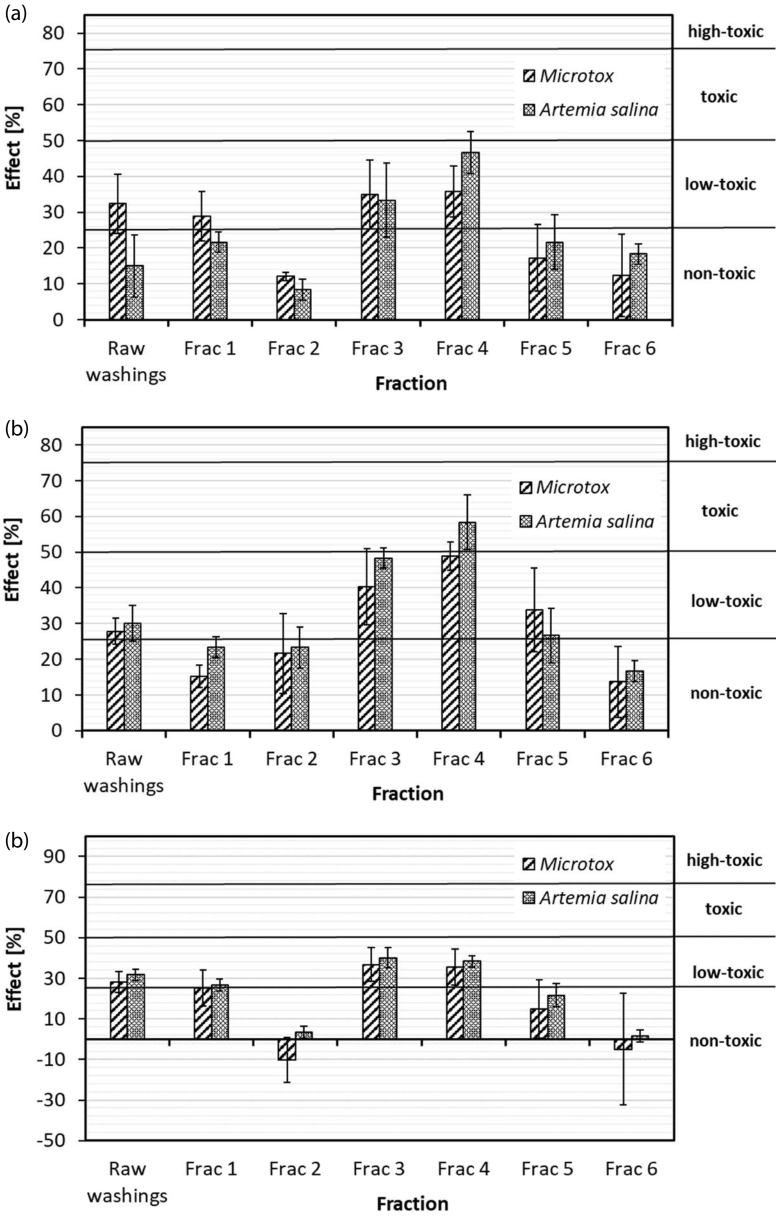

Fig. 5. Comparison of washings toxicity from systems: (a) swimming pool (SWP), (b) hot tub (HT), and (c) common circulation of toddler pool and hot tub (TP + HT, respectively).

that there was a significant share of halogenated organic compounds.

- The relationship between the function/type of circulation and the concentration of TOC was demonstrated, with the highest concentrations of TOC being in the samples taken from the swimming pool, and the lowest in the hot tub. The use of ultra- and nanofiltration membranes with various resolution properties allowed for the isolation of permeates and retentates from apparent molar masses: >200; <200; 200–30; <30 kDa; 30 kDa–300 Da; <300 Da.
- There was a significant share of the impurity fraction below 300 Da. The concentrations of TOC and the sum of absorbable organic halogens were in the range from 0.70 to 0.93 mg C/L and from 0.17 to 0.47 mg Cl/L, respectively. None of the analyzed samples showed any toxic effects.
- No significant correlation was found between TOC concentration and turbidity or absorbance in UVA$_{254}$ ultraviolet. This is important information because the value of ultraviolet absorbance is often equated with the concentration of DBPs.
- There was no link between the increased level of TOC and the increased toxic effect.
- An increase in the toxic effect was noted for the 200–30 kDa and <30 kDa fractions, with the obtained values being within the low toxicity range.
- The membrane fractioning process can be used to obtain solutions and to characterize them by apparent molar

mass. It has to be kept in mind that in a dead-end filtration system, some impurities can block membrane pores and reduce their diameter, which may result in errors in the analysis.

- Expanding the knowledge about the nature and size of pollutants in the swimming pool water gives a signal that the current swimming pool water treatment methods need to be revised and modernized.

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