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REVIEW ARTICLE

HEALTH RISK AS A CONSEQUENCE OF EXPOSURE TO TRIHALOMETHANES IN SWIMMING POOL WATER

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ABSTRACT

The article presents the formation and toxicity of trihalomethanes (THMs), substances belonging to Disinfection By-Products (DBP), formed as a result of pool water chlorination. Concentration of THMs in pool water has been standardised in Poland since recently. THMs concentration in pool water depends on multiple factors, mostly the method of water disinfection, including chlorine or organic substance (TOC) concentration. Apart from that, the level of exposure of swimmers to the toxic effect of THMs is affected by their content in the air of swimming pool halls, intensity of swimming as well as time of stay in the indoor swimming pool area. The water and air temperature as well as number of swimmers and time of their staying in pool have also significance influence on THMs concentration. In order to decrease the quantity of THMs in pool water, alternative disinfection agents are applied. Additionally, an efficiently operating pool ventilation system as well as proper water treatment method are also important. Because THMs are produced from organic material under the influence of the chlorination, the users can have an impact on decrease of the THMs concentration in pool water, for instance by taking a shower prior to entering the pool or by wearing a swim cap. The results of studies conducted in 2015 showed that the quantity of THMs in pool water depends on type of the pool (indoor, outdoor), water replacement frequency, water treatment system, chlorine dose and TOC content. In most collected samples, the THMs concentration exceeded the admissible norm (100 μg/L).

Key words: *water, swimming pools, trihalomethanes, THMs, toxicity*

STRESZCZENIE

W artykule omówiono powstawanie i działanie toksyczne trihalometanów (THM), związków należących do tzw. *Disinfection By-Products* (DBP), powstających w wyniku chlorowania wody w nieckach basenowych. Od niedawna w Polsce normuje się stężenie tych związków w wodzie basenowej. Stężenie THM w wodach w obiektach basenowych zależy od wielu czynników, głównie od sposobu dezynfekcji wody, w tym stężenia chloru oraz substancji organicznych (TOC). Poza tym na stopień narażenia pływaków na toksyczne działanie THM ma ich zawartość w powietrzu hali basenowych, intensywność pływania oraz czas przebywania na terenie pływalni. Ważna jest też temperatura wody i powietrza oraz ilość osób korzystających z basenu w danym czasie. W celu zmniejszenia ilości THM w wodzie basenowej stosuje się alternatywne środki dezynfekcji. Poza tym ważny jest sprawnie działający system wentylacji hali basenowej i odpowiedni sposób oczyszczania wody. Ponieważ THM są wytwarzane z udziałem substancji organicznych pod wpływem chlorowania, korzystający z basenów mogą wpłynąć na obniżenie poziomu THM, np. poprzez noszenie czepków oraz skorzystanie z prysznica przed wejściem do wody. Przeprowadzone w 2015 roku badania wykazały, że ilość THM w wodzie basenowej zależy od wielu czynników, w tym rodzaju basenu (kryty, odkryty), częstości wymian wody, rodzaju systemu jej oczyszczania, dawki chloru oraz zawartości TOC. W większości pobranych próbek stężenie THM przekraczało dopuszczalną normę (100 μg/L).

Słowa kluczowe: *woda, baseny, trihalometany, THM, toksyczność*

INTRODUCTION

Most common halogen derivatives of hydrocarbons, the so called halomethanes are formed in water treated for the purpose of disinfection, usually when chlorine compounds are used. THMs belong to the so-called water disinfection by-products (DBPs), which are formed in swimming pool water and ambient air. It is known that there are over 600 of such compounds. They were divided into 3 main groups: trihalomethanes (THM),

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chloramines and haloacetic acids (HAAs). They are characterized by different toxicity. Usually in THMs contained in swimming pool water, the highest number of chloroforms (CHCl3) is indicated, due to the use of chlorine for water disinfection. The main representative of chloramines present in pool water is the trichloramine NHCl3 - irritating to the skin and eyes - which is responsible for the "chlorine" odour in the pool facilities. The third group, which is haloacetic acids (HAAs) consists of non-volatile compounds, thus they remain in the pool water. Most frequently compounds with chlorinated derivatives of methane (THMs), which are determined, are chloroform (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM), bromoform (TBM). The THMs formation precursors in water are organic carbon of natural or anthropogenic origin. Therefore, in the analysis formation process and the concentration of their organic precursors in water should be take into account. Not all organic compounds in the water have the ability to react with chlorine, usually water soluble compounds as Dissolved Organic Carbon (DOC) [36].

The problem concerning formation of THMs in drinking water has been widely examined [3, 7, 17, 20]. In accordance with Polish Law, the content of these compounds in drinking water must not exceed 100 μg/L [28]. The research study indicates that the content of THMs in swimming pool waters is usually much higher than the one specified in the standard for drinking water, due to much higher degree of chlorination of swimming pool water and raised content of organic compounds. In the case of pool water, the THMs precursors are mostly: urea, ammonium ions, α-amino acids and creatinine, introduced into the water by people bathing [14, 25].

In Poland in 2015 a new law regulation has been in force ordering of monitoring of THMs in swimming pool water and limit values for these compounds have been specified [29]. Limit values for these compounds have been established: the concentration of THM should not exceed 100 μg/L and chloroform of 30 μg/L, with the exception of water in children pools, where the concentration of chloroform can not exceed 20 μg/L. This is due to the highest THM toxicity in relation to the other groups. In many countries, despite the lack of guidelines for swimming pool water, it is assumed that THM concentrations should be at the same level as the standards for drinking water indicated (100μg/L) in accordance with Directive 98/83/EC [17]. Other European countries have already established individually the maximum value of THMs in swimming pool water, and in the case of Germany it is (20μg/L) and in Denmark (50 μg/L) [17, 18]. The World Health Organization (WHO) establishes different guideline values for each THMs: 300 μg/L for TCM, 60 μg/L for BDCM, and 100 μg/L for both CDBM and TBM [18].

The aim of the article was to describe the sources and the impact of THMs for swimming pools users and the possibility of reducing exposure to these compounds. The purpose of this review article was beginning of the study monitoring water quality in swimming pools in Opole Region [26]. The obtained results allowed for evaluation of water quality and allow to reduce of hazardous compounds concentration in water, as a consequence increase the safety of swimmers.

TOXICITY OF THMs

In 1976, the US National Cancer Institute has published for the first time the information that chloroform, being present in the drinking water, is carcinogenic to rodents. Subsequent research studies suggested that chlorinated drinking water may be associated with increased risk of developing bladder, rectal and colon cancers [3]. Based on the results of toxicity tests on drinking water in India, *Mishra* et al. [20] have stated that THMs being entered through oral and inhalation route have direct impact on human health. According to the authors [20], THMs penetration from drinking water through the skin, for example during bathing was insignificant. A similar study was conducted in Thailand [24]. It was proven that the greatest risk caused by drinking the water is THMs absorption through oral route, then through skin, and lastly through inhalation. The International Agency for Research on Cancer (IARC) classifies chloroform and bromodichloromethane as compounds that are probably carcinogenic to humans (Group 2B) [27]. Recent epidemiological data indicate that exposure to THMs is associated with an increased risk of bladder cancer [34]. It is also proven that THMs are teratogenic [12, 22, 34]. The direct negative impact of THM contained in pool water on the health of pregnant women and the risk to the foetus was not proven [34]. It was reported that carcinogens contained in the pool water, including THMs, should be considered in the etiology of melanoma [34]. It was proven that THMs from pool water may cause bladder cancer, as well as THMs from the drinking water [27]. The presence of biomarkers of genotoxicity was found in the urine of swimmers utilizing pool facilities. However, in the case of swimmers, it turns out that the greatest threat from THMs is its content in the ambient air of swimming pools and not in the water [34]. It is confirmed by Erdinger et al. [10], who demonstrated that the content of THMs in swimmers' blood is correlated with their content in the ambient air of swimming pools and not with the content in the water. They found a direct impact of swimming intensity on THMs accumulation in the organism of swimmers. The authors [10] suggested that THMs are absorbed mainly by inhalation rather

than through the skin or by accidental ingestion of water, while swimming. This is confirmed by tests performed among 183 indoor pools in Korea [13]. There was discovered that the risk caused by THMs received orally and through skin from the pool water is negligible, and swimmers are exposed to uptake these compounds by inhalation. Other conclusions were reached by *Lindstrom* et al. [15], who stated that the main way of absorbing THMs by swimmers is through the skin (80%). Despite of swimmers, people working in swimming pools (lifeguards, instructors and technical staff) are largely exposure to THMs. Such exposure is prolonged and may cause adverse health effects expressed in respiratory diseases, including asthma, skin problems and eye irritations [34]. Another group vulnerable to negative effects of THMs arisen from water pools are swimmers, especially competitive ones. In research tests concerning people benefiting from swimming pools, it was stated that the presence of all four forms of THMs in the exhaled air; in their blood only chloroform was detected, and in the urine, the presence of chloroform bromodichloromethane was detected [34]. It may suggest that THMs absorbed by inhalation in the majority are removed together with the exhaled air and a small amount of them is transferred into the blood and then into the urine. After getting into mammalian blood, THMs are quickly metabolized and excreted [24].

It is presumed that some of the symptoms occurring in swimmers' organism, such as irritation of eyes, skin or respiratory problems may be caused by chlorine or chloramine present in the ambient air of swimming pool, rather than in the presence of THMs [34]. This is confirmed by tests in 334 lifeguards working at indoor swimming pools in France and in more than 600 employees of swimming pools in the Netherlands and the USA [34]. However, in the Italian research studies, a direct relationship between the content of THMs in the exhaled air in workers of swimming pools and the occurrence of respiratory diseases has been proven [34]. Regardless the type of irritants being present in the air, there are more incidence of respiratory diseases among swimmers than in other sportsman. Due to the suspicion that swimmers are exposed to THMs contained in the pool water and in the air, numerous studies on the effects on children using the pools were performed [34]. Alarming results of the research were received by Spanish researchers, who found that children attending the swimming pools had four times higher uptake of THMs, compared to non-swimming children that means not using the pools [11]. It is also suspected that the use of swimming pools can aggravate asthma symptoms in children [34], however this effect has not been definitively confirmed. Despite this, the Belgian Government, on the basis of the precautionary principle, does not recommend swimming in chlorinated pools to children under one year of age, especially children with atopic dermatitis and those whose parents have asthma [34].

SOURCES OF EXPOSURE OF SWIMMERS TO THMs

The main source of exposure of swimmers to the THMs is the pool water. The harmfulness of THMs depends on the route of their absorption. Scientific research has not stated clearly which sources of exposure are most dangerous for the swimmers. Some reports claim that THMs are absorbed via the respiratory route due to the high volatility of these compounds [12, 26]. It turns out that THMs absorbed via the respiratory route are removed in most part together with the exhaled air [24]. The scientists argue whether the main source of penetration of THMs from the pool water to the human body is the skin, respiratory tract or accidental swallowing [13, 15, 24].

The amount and impact of the THMs exposure may be influenced by many factors as well as the type and dose of disinfectant, and consequently the THMs concentration in water, the number of swimmers, temperature of water and air, system of ventilation in the building, duration of swimming, and the turbulence in the water generated by moving-water features such as fountains, water slides, wave pools, and hot tub jets [9, 25]. Additionally, the THMs concentration in pool water is affected by the swimmers themselves. They introduce various contaminants to the water, such as epithelial particles, sweat, urine as well as microorganisms. According to *Wyczarska-Kokot* [35], one person can introduce up to a billion of bacteria to the pool water, including pathogens. In case of high attendance rate, this could lead to quick spread of an infection. Thus, the most important element of the swimmers' safety is proper method of water disinfection. Therefore risk management strategies should be developed that minimize THMs exposure, without compromising disinfection efficiency. The presence of organic matter from swimmers in the form of hair products, lotion, mucus, skin excretions and urine are included in THMs precursors [9, 14]. Urea is also a precursor for formation of toxic chloramines. As claimed by *Ratajczak* [25], the amount of urea on human skin is ca. 100-160 mg. Therefore, the more people swim, the more urea is introduced to the water by them and, thus, the count of disinfection by-products and emission of these compounds increase. The alternative disinfection methods that are to lower the DBP formation potential in the pool water include use of ozonisation or UV radiation. It turns out, however, that UV radiation decreases the amount of chloramine in pool water, concurrently increasing THMs concentration [5]. Ozonation is a water

disinfection method combined with chlorination due to the short term of ozone effectiveness (20-30 minutes). It turns out that ozonisation of water also causes formation of less harmful substances, e.g. aldehydes [21]. Other pool water disinfection methods include also brominating or electrochemical methods (*Electrochemically Generated Mixed Oxidants*). However, it was proven that they cause synthesis of much more toxic brominated THMs [13, 16, 36]. the disadvantages of pool water brominating include also causing of more frequent toxic effects in the form of skin inflammation or eye irritation. Brominated organic compounds are more cytotoxic and mutagenic than chlorinated compounds. Another method of disinfection of the pool water, currently checked in the USA, is use of silver or copper nanoparticles [1]. Preliminary studies confirm decrease of the count of THMs formed in water as well as minimisation of eye or skin irritation effects. When assessing this disinfection method, one must be cautious since there is not enough data currently in relation to toxicity of nanoparticles or their effect on human body.

THMs CONCENTRATION IN POOL WATERS

The THMs concentration depends on the method of pool water disinfection. For the indoor pools where chlorination was used, the concentration of these compounds varies significantly. *Marco* et al. [19] determined THMs concentration in Spanish pools within the range from 35-75 μg/L , whereas *Lourencetti* et al. [16] - within the range from 28-84 μg/L. In both publication higher concentration of THMs in water tretaed by bromination was found. In the Italian studies carried out by *Righi* et al. [27] at 24 indoor pools, the THMs concentration range was very wide (6.8-134 μg/L). A similarly range of results was obtained by *Silva* et al. [30] who examined water at 30 Portuguese swimming pools (10-155 μg/L). *Chu* et al. [6], examining 8 indoor swimming pools in London, determined high THMs concentrations (mean 132.4 μg/L, min. 57 μg/L, max. 223 μg/L). The differences resulted from, inter alia, size of the swimming pool facility and number of swimmers. *Peng* et al. [23], in the course of investigation conducted at two swimming pools in Germany, determined a low THMs concentration level of 25.6 μg/L. In Germany, the permissible THMs concentration is only 20 μg/L. Multiple water quality tests at the indoor pools were conducted in Quebec in Canada: 17.5-113.5 μg/L [31], 12.9-215 μg/L [9], 41.3-132.4 μg/L [33].

There is not much data regarding Polish swimming pools. The studies of *Szczyglowska* et al. [32] conducted at a large pool complex, the THMs concentration was examined in several pool basins. The THMs concentration in the supply water was determined by the authors [32] at the level of 1.2 μg/L, and at the outlet from each basin - from 17 μg/L to 28 μg/L. The studies by *Czajka* et al. [8] assessed the effect of chlorination of brine at a therapeutic pool on its THMs content. The authors determined the THMs concentration within the rage from 41.7-68.4 μg/L in fresh water and 72.2-100.8 μg/L upon 2 months of use. In the course of own studies conducted in 2015 at five indoor and five outdoor swimming pools in the Opole region, THMs count was determined in a very wide range, accordingly: 27-279 μg/L and 15-551 μg/L [4, 26]. It was stated that the THMs share was the lowest upon replacement of water in the pool basins. The concentration of these compounds increased along with operation. It was also stated that the THMs concentration in the indoor pool water depended on the type of employed water treatment system. The system based on the gravel-sand-anthracite bed proved to be the least advantageous. Other facilities had filters based on diatomaceous earth. The situation in case of outdoor pools is slightly different. Some of them have been functioning for over 80 years. Most of them had no water recirculation and filtration system, except for one. Their use consists mostly in filling the pool basin with underground water, manual dosing of chlorine compounds and water quality monitoring. In case of its significant worsening, the pool basin was emptied and - upon cleaning - refilled with fresh water. Higher concentration of THMs in outdoor pool water is connected, most probably, with the higher level of chlorination of this water and increase share of organic matter in relation to waters at indoor swimming pools. The research found that the dominant compound from the THM group was chloroform and bromoform [26]. The studies are planned to be extended with a greater number of facilities and air quality at the indoor pools in order to monitor the level of water contamination and identification of potential sources of formation of these compounds.

REDUCTION METHODS OF NEGATIVE EFFECT OF THMs ON PEOPLE

The most important factors having an impact on formation of toxic compounds in the pool water is the amount of organic matter introduced by the persons using the pools. The more people swim, the more urea is introduced to the water by them and, thus, the count of THMs increases. Decrease of the amount of organic compounds introduced by the swimmers could be obtained through introduction of the obligatory shower bath prior to entering the pool. In addition to the bath prior to entering the pool, recommendations regarding wearing swim caps are also note-worthy since it is believed that hair is the number one source

of contamination [25]. The amount of organic matter being the DBP precursor is reduced during filtration of the pool water. Therefore, use of modern filtration methods as well as their proper operation are important. Filtration and flocculation are used in most swimming pools for water treatment on sandy and diatomaceous beds. The combination of membrane filtering and intensive oxidation gives better effects, eliminating most DOC and microorganisms - as compared to the traditional methods [36]. Pool water cleanliness control methods, e.g. through replacement of acids for water pH regulation with CO_2 gas, are also suggested [12].

A very important issue in the context of THMs toxicity is proper design of the ventilation systems. *Ratajczak* [25] suggests that the ventilation system should operate only in open air to ensure removal of harmful gaseous compounds. This solution, however, is disadvantageous due to use of high amounts of energy by the pool facility.

In order to assess the potential of THMs formation in the pool water, *Luks-Betlej* and *Bodzek* [17] recommend continuous monitoring of water in terms of temperature, pH, free and residual chlorine, total organic carbon (TOC) content and number of swimmers. An additional element is strict observance of the chlorine concentration standards for pool water. Due to the need to meet the required sanitary effects, the chlorine concentration in pool waters can be sometimes slightly exceeded in relation to the recommended level (0.3-0.6 mg/dm^3), especially in outdoor pools, as proven by own research conducted at the swimming pools in Opole region [26]. The scope of project [26] implementation covers examination of pool water quality at selected indoor and outdoor swimming pools in Opole region. This allowed to determine the actual water quality at the swimming pools of the voivodship. The studies will allow in the future to take actions aimed at reduction of these harmful compounds in the water which, in consequence, will improve safety for pool users.

SUMMARY

For the persons using the swimming pools, the most important thing is to ensure sanitary safety of water. The compounds belong to the Disinfection By-Products (DBP) group, i.e. trihalomethanes (THMs) are subject to standardisation. These are toxic compounds, and in case of two of them it has been proven that they have carcinogenic and mutagenic effect. THMs concentration in pool water depends on multiple factors, mostly the method of water disinfection, including chlorine or organic substance concentration. Apart from that, the level of exposure of swimmers to the toxic effect of THMs is affected by the intensity of swimming as well as time of stay in the indoor swimming pool area, due to their content in the air of swimming pool halls. Additionally, the water and air temperature as well as number of persons using the pool at the given time are also of significance. In order to decrease the quantity of THMs in pool water, different methods are applied such as alternative disinfection agents, with the best effects obtained by means of ozonisation combined with chlorination. Additionally, an efficiently operating pool ventilation system decreasing the concentration of these compounds in the air is also important. One of the most important factors is the proper method of water treatment. The best solutions proves to be combination of membrane filtering and intensive oxidation. People using pools can have an impact on decrease of the THMs concentration in pool water themselves, by wearing a swim cap, limiting the hair contact with water as well as by taking a shower prior to entering the water, decreasing the microorganism count and amount of urea introduced to the pool. The results of studies conducted in 2015 showed that the quantity of THMs in pool water depends on multiple factors, including pool type (indoor, outdoor), water replacement frequency, water treatment system, chlorine dose and TOC content. In many collected samples, the THMs concentration exceeded the admissible norm (100 μg/L). This is a troubling result. Therefore, it is necessary to commence the actions aimed at decrease of THMs concentration in pool waters.

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Conflict of interest

The authors declare no conflict of interest.

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