Disinfection by-products monitoring in water of selected outdoor swimming pools in Opole Voivodship

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Abstract. The aim of this study was to determine the level of disinfection by-products in selected outdoor swimming pool in the Opole Voivodship. The authors paid special attention to the determination of the concentration of trihalomethanes (THMs), which are formed during disinfection in water. Five outdoor swimming pools were selected in five different cities located in Opole Region. The level of trihalomethane (THM) concentrations in the analyzed waters was found to be in the wide range from 15 to more than 550 µg/L. The dominant compound of THMs was chloroform because of chlorine application in the disinfection method.

1 Introduction

Disinfection forms a mandatory process for the public indoor and outdoor swimming pools. Chlorine-based disinfectants are included among the most frequently applied disinfectants and oxidizers for swimming pool treatment.
In contact with swimming pool water, these substances produce a variety of disinfection byproducts (DBPs), such as trihalomethanes (THMs), whose concentration needs to be regulated in swimming pools water. The amount of DBPs that are formed in pool water is influenced by several factors, including free residual chlorine, number of swimmers, water temperature, total organic carbon (TOC), water resource, and pH [1-8]. World Health Organization (WHO) data point out that the toxicity of those hazardous substances introduced by the inhalation route is much higher than by ingestion or through dermal contact. Therefore WHO recommend a maximum concentration of 100 mg/L of THMs for all types of swimming pool waters. Additionally, the International Agency for Research on Cancer (IARC) classified some THMs (chloroform and bromodichloromethane) as potentially carcinogenic to humans (group 2B) [8].
In Poland standards of swimming pool water quality are regulated by the national law, i.e. by the Regulation of Minister of Health on the requirements to be met by water in swimming pools [9]. On the list of the many physico-chemical parameters of water, the parameters relating to DBPs are included as well.
Selected parameters associated with the formation DBPs in swimming pool water are summarized in Table 1. In accordance with WHO recommendations, the maximum level of THMs should not exceed 100 µg/L, wherein chloroform concentration cannot be higher than 0.03 mg/L for all pool types, except for water in the pool basin using by infants. In such facilities maximal chloroform concentration must be lower than 0.02 mg/L.
A variety of studies have been disseminated on the presence of DBPs in swimming pools. Some reports [10-14] have served to offer an account of the total of THMs, or identified only chloroform [15-18]. There are also publications which include measurements that have been carried out with regard to pool water on a reduced scale or with samples generated in laboratory-scale simulations [17-21]. Unfortunately little attention has been paid to investigating the seasonal occurrence of DBPs in outdoor swimming pool waters.

Table 1. Selected physico-chemical requirements for swimming pool water according to Regulation of Polish Minister of Health [9].

Parameters	Unit	Water introduced into the pool basin in the circulation system	Water in the pool basin	Water in the pool basin equipped with aerosol devices	Water in the pool basin using by infants
Cl (bound)	mg/L	0.2	0.3	0.3	0.3
Chloroform	mg/L	0.03	0.03	0.03	0.02
ΣTHM	µg/L	100	100	100	100

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2 Materials and methods

Five outdoors swimming pools located in various cities located in Opole Voivodship were selected for the study. The selection of the study facilities was affected by the possibility of gaining permission for conducting the tests. A lot of outdoor swimming pools operate in the Opole Voivodship, some of them have been in operation for over 80 years. Many of them do not include a recirculation or filtration systems. The operation of these facilities involves only filling the basin using underground water, manual dosing of chlorine compounds and periodic monitoring of biological water quality. With significant deterioration of water quality, the basin is emptied and after cleaning, filled with fresh spring water. We can assume that this solution leads to formation of DBPs. The technical parameters of five selected research facilities are summarized in Table 2.
Water samples were collected during the summer season at intervals of two weeks; each object was tested four times. All water samples were taken at approximately 30 cm under the water surface. Amber glass bottles (100 mL) with glass screw caps were used for the collection of the treated water. The jars were completely filled to avoid the evaporation of volatile compounds. Samples were not stabilized by addition of any reagents. Samples were stored at <4ºC during transport to the laboratory. Immediately after sample collection (1-2h), THMs were extracted using liquid-liquid extraction with penthane (10:1, v:v) at room temperature. Samples were shaken manually (1 min) and extracts were stored in amber glass vials at <4ºC until analysis was performed not later than 14 days after the date of sampling. Sampling, extraction and analysis procedures were performed according to the PN-EN ISO 10301:2002 standard. Simple standard of THM (TCM, BDCM, CDBM and TBM) - concentration of 2,000 mg/dm^3 in methanol (Restek) was used.
With individual standards a mixture of THMs and methanol (Merck, GC - grade) was performed.
An intermediate standard stock solution of THMs 20 µg/dm^3 was obtained by diluting the THM standard mixture methanol and was stored at -18ºC. Calibration standards were prepared from standard stock solution in penthane (Merck, UniSolv(R)). Sufficient linearity was obtained for all THMs with the correlation coefficients r>0.995.
Separation and identification of THMs was carried out with an Agilent Technologies 7890B gas chromatograph equipped with a micro-electron capture detector (µECD) and a capillary column (Ultra Inert DB-5MS, 30 m×250 mm×0.25 mm). Helium was used as the carrier gas with a flow rate of 1 mL/min, and nitrogen was used as makeup gas with the flow rate of 30 mL/min. The oven was held at 35ºC for 20 min, then it was ramped at 10ºC/min to 150ºC, held for 3.5 min at 150ºC. The injector and detector temperatures were 200ºC and 300ºC, respectively. The injection was operated in a splitless mode.

3 Results and discussion

The concentration of trihalomethanes in water was characterized by a considerable variability in the examined pools. A wide range of concentrations expressed in terms of the total of these compounds was determined, i.e. 15-551 µg/dm^3 (Table 3). The lowest concentration ∑ THMs was found in the samples derived from the pool no. 3, as it was equal to 116 mg/L. Among the facilities applied in this analysis, the swimming pool no. 3 forms the most modern of them all, as it underwent a thorough upgrade in 2006. In this facility, water filtration is used, as it probably affects the limitation of the number of precursors, and thus the formation of THMs (Table 3).
The highest concentration in terms of the total of trihalomethanes was recorded in the water of facility no. 2, as it was equal to 338 µg/L, and the concentration of the total THMs for pool no. 1 was equal to 158 mg/L and

Table 2. Selected technical and technological parameters of outdoor swimming pools.

Technical data of investigated facilities	Research objects				
	No. 1	No. 2	No. 3	No. 4	No. 5
Volume of the swimming pool, m^3	ab. 1,200	ab. 1,200	ab. 1,200	ab. 1,200	ab. 1,200
Basin dimensions (length *x* width), m	50 x 22	50 x 20	50 x 20	50 x 20	50 x 20
Disinfection method	NaClO	NaClO	NaClO	NaClO	NaClO
Recirculation and water treatment system	none/complete replacement of water	none/complete replacement of water	filtration and recirculation	none/complete replacement of water	none/complete replacement of water
Other data	built in the 1930s	no data	built in 1950s after a complete refurbishment in 2006	built in the 1970s	built in the 1970s

in the facility no. 4, it was 128 μg/L, compare to 274 μg/L in the facility no. 5. It is not possible to determine a reason to explain the differences in the concentrations of trihalomethanes in the individual pools. We can assume that the content of these compounds is affected by the number of people who use the pools, but this statement could not be confirmed because there is a lack of data regarding the number of swimmers in the examined facilities in the summer. Hence, we can only assume that the level of THMs increases with time, starting from filling the pools and throughout the summer season, especially for facilities that do not include a water treatment system. However, no such relationship was observed.

As we know, the concentration of THMs in water is affected by many factors, not just the content of precursors and the degree of its chlorination, but also water pH, insolation and air temperature [1-3,12,13]. Thus, we can assume that the reason for the high variability of THMs is associated with the difference between the quality of water that is applied to fill the pools. In each of the examined facilities, water came from a different source.

Among the investigated THM_S, chloroform (TCM) was responsible for the highest ratio, as in the pool no. 1 the chloroform concentration was equal to 58 μg/L. In the pool no. 4 the level of chloroform was at a level of 93 μg/L. Pool no. 5 was characterized by the highest levels of the examined parameters, as the concentration of TCM was equal to 223 μg/L in it.

In the case of pool no. 2, a high concentration of bromoform was also recorded, at a level that was similar to the concentration of chloroform. This results could be due to the higher concentration of bromides in the water supplying the pool basin.

The total organic carbon (TOC) determined in the waters of the examined facilities did not differ significantly, i.e. 2.1–3.8 μg/dm^3. The concentration of TOC in the examined waters was found not to affect the concentration of trihalomethanes.

For the purposes of gaining comparative results, the data regarding outdoor swimming pool was compiled with data for indoor pools located in the Opole Voivodship, with a note that the measurements were carried out at the same time. Table 4 shows the mean results for chloroform and total THMs coupled with the data regarding the range of minimum and maximum concentrations for five indoor and outdoor pools. As we can see, the values recorded in the indoor facilities were considerably lower. Indoor pools are modern facilities that contain water treatment systems, which affects THMs levels in waters.

Table 3. The results of the analysis of THMs in 5 selected outdoor swimming pools waters in Opole Voivodship.

Parameters	Research object				
	1	2	3	4	5
TCM, μg/dm^3	136±78 (57-214)	153±75 (41-194)	58±21 (37-78)	92±30 (58-116)	223±153 (15-372)
BDCM, μg/dm^3	7±1 (5-8)	5±4 (3-10)	1±0.1 (<0.1-1)	8±2 (5-9)	10±7 (<0.1-16)
DBCM, μg/dm^3	1±0.1 (<0.1-1)	1±1 (<0.1-2)	1±0.1 (<0,1-1)	<0,1	1±0,1 (<0.1-2)
TBM, μg/dm^3	14±9 (4-20)	179±126 (54-351)	57±42 (21-114)	28±11 (19-40)	40±62 (<0.1-130)
∑THM, μg/dm^3	158±79 (83-241)	338±148 (233-551)	116±60 (59-190)	128±42 (82-164)	274±210 (15-518)
TOC, μg/dm^3	3.0±0.3 (2.7-3.2)	2.1±1.5 (1.1-3.2)	3.5±0.4 (3.2-3.8)	3.8±0.8 (3.2-4.4)	3.7±0.7 (3.2-4.3)

Table 4. Results of water samples from the selected outdoor and indoor pools in Opole Voivodship.

Parameter	Outdoor pools		Indoor pools [10]	
	Concentration, μg/dm^3	**The proportion of samples exceeding the norm value ***	**Concentration, μg/dm^3**	**The proportion of samples exceeding the norm value ***
Chloroform (TCM)	132±63 (15-372)	94%	61±47 (26-208.2)	76%
∑THM	203±98 (15-551)	78%	122±74 (28-279)	57%

*****- 100 mgTHM/dm^3 and 30 mgTCM/dm^3 according to [9]

4 Conclusions

By-products of water treatment are formed in the waters of outdoor pools in Opole Voivodship, mostly ones containing chloride derivatives of methane and ones taking the form of chloroform. The identified contamination levels in each of the analyzed outdoor pools exceed the values specified in the regulation of the Minister of Health stipulating the requirements regarding swimming pool water. It is significant that the tests were carried out in the summer season preceding the implementation of the above regulation as valuable source of information was gained for the operators of the examined facilities. All examined facilities had to implement corrective action plans, the outcome of which involved the decrease of the total concentration of THMs to less than 100 μg/dm^3. The results obtained and reported in this paper do not deviate substantially from the results of studies reported in scientific journals. Thus, we can state that the maintenance of a low concentration level of water disinfection by-products is a difficult task – especially in facilities where the only method applied to ensure microbiological safety of water involves batching chloride compounds. The type of pool appears to have an impact on the levels of recorded DBPs. The measured concentrations of THMs are greater in outdoor pools.

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