



Occurrence and simulation of trihalomethanes in swimming pool water: A simple prediction method based on DOC and mass balance



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ARTICLE INFO

Article history:

Received 7 August 2015

Received in revised form

28 October 2015

Accepted 30 October 2015

Available online 9 November 2015

Keywords:

Trihalomethanes simulation

Disinfection by-products

Indoor swimming pool water

Chlorination

THM

DOC

ABSTRACT

Trihalomethanes (THM) are the most typical disinfection by-products (DBPs) found in public swimming pool water. DBPs are produced when organic and inorganic matter in water reacts with chemical disinfectants. The irregular contribution of substances from pool visitors and long contact time with disinfectant make the forecast of THM in pool water a challenge. In this work occurrence of THM in a public indoor swimming pool was investigated and correlated with the dissolved organic carbon (DOC). Daily sampling of pool water for 26 days showed a positive correlation between DOC and THM with a time delay of about two days, while THM and DOC didn't directly correlate with the number of visitors. Based on the results and mass-balance in the pool water, a simple simulation model for estimating THM concentration in indoor swimming pool water was proposed. Formation of THM from DOC, volatilization into air and elimination by pool water treatment were included in the simulation. Formation ratio of THM gained from laboratory analysis using native pool water and information from field study in an indoor swimming pool reduced the uncertainty of the simulation. The simulation was validated by measurements in the swimming pool for 50 days. The simulated results were in good compliance with measured results. This work provides a useful and simple method for predicting THM concentration and its accumulation trend for long term in indoor swimming pool water.

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1. Introduction

Water in public swimming pools is practically continuously disinfected in order to control the pathogenic microorganisms and to guarantee the hygiene. To date chlorine-based chemicals are still the most common and practiced disinfectants, including chlorine gas, sodium/calcium hypochlorite, or sodium hypochlorite produced through electrolytic generation (Black and Veatch, 2010). The negative health effects which have been associated with the consequently formed disinfection by-products (DBPs) from the reaction between chlorine and organic matters in water have driven much attention in recent years (Richardson et al., 2007; Villanueva et al., 2007).

Pool water chlorination regulation and guidelines vary from country to country. The term “free chlorine” is practically defined as the sum of available HOCl, OCl⁻, and Cl₂ (aq). The New South Wales Ministry of Health, Australia recommends a free chlorine

concentration ≤2 mg/L for indoor swimming pool water (pH-value < 7.6) (NSW, 2013). The province of British Columbia, Canada, mentioned that the free chlorine level must be equal or lower than 0.5 mg/L (temperature ≤ 30 °C) or lower than 1.5 mg/L (temperature > 30 °C) (BC Reg 296/2010, 2010). In Germany according to the German Pool Water Standard DIN-Norm 19643-1 (DIN, 2012a) the free chlorine in swimming pool water generally should be maintained at 0.3–0.6 mg/L and for hot whirlpool at 0.7–1.0 mg/L to achieve a sufficient disinfection capacity. A maximum concentration at 1.2 mg/L is allowed for certain operation conditions.

DBP levels in swimming pool water are higher than in drinking water (Kanan and Karanfil, 2011) and induced more genomic DNA damage than the source tap water (Liviak et al., 2010), mainly associated with chlorination at higher water temperature (25–35 °C) (Simard et al., 2013). The problem is particularly more evident in swimming pool water, where the treated water is almost entirely recirculated. Here, the substances which cannot be removed by the treatment will accumulate (Barbot and Moulin, 2008; Simard et al., 2013). Trihalomethanes (THM) are the most

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Nomenclature

A	water surface area of swimming pool
DBP	disinfection by-product
DOC	dissolved organic carbon
HAA	haloacetic acids
H _C	Henry's law constant
k	removal coefficient of THM
k _a	air-phase mass transfer coefficient
k _w	water-phase mass transfer coefficient
K _a	overall mass transfer coefficient in the air phase
K _w	overall mass transfer coefficient in the liquid phase
K _{wa}	overall water–air mass transfer coefficient

m	mass
Q _{FW}	filling water inflow
Q _{TM}	volumetric flow rate of pool water treatment
R _C	specific production ratio of THM from DOC
t	time
THM	trihalomethanes
THMFP	maximum formation potential of THM
V _{Pool}	total water volume in the swimming pool
X _{THM}	THM removal ratio during one passage of the pool water treatment process
ρ _{DOC}	DOC concentration in swimming pool water
ρ _{THM}	THM concentration in swimming pool water

typical organic DBPs in both drinking and swimming pool water. Volatile DBPs like THM can be taken up via inhalation, dermal adsorption and ingestion. Compared to intake of tap water, gastrointestinal exposure in pool water and skin exposure during showering, skin exposure while swimming is the main intake route of THM contributing cancer risk (Panyakapo et al., 2008). Usually chloroform is the predominant THM formed, contributing an average of more than 95% by weight to the total THM (Bessonneau et al., 2011; Simard et al., 2013). Other THM compounds such as bromodichloromethane, dibromochloromethane and bromoform, are normally found in much lower concentrations than chloroform. Practically the total THM concentration is the sum of different THM calculated and given as chloroform. According to the German Pool Water Standard (DIN, 2012a) the recommended concentration for THM in swimming pool water is 20 µg/L.

Various studies have reported a wide variation of THM occurrence in swimming pool water. However, THM concentration can vary significantly in pool water over one day, weeks and months (Kristensen et al., 2010). Intermittent sampling can be insufficient for investigation of the formation mechanism in the whole swimming pool water system. Comprehensive understanding of THM formation, occurrences and their variability is essential for DBP study in swimming pool water. THM formation is affected by the disinfectants, disinfection conditions and character of water sources. Natural organic matter (NOM) from humic origin is generally accepted as precursors for DBPs (Barrett et al., 2000; Krasner et al., 2006; Rook, 1974), which is brought into swimming pool with the filling tap water. Additionally pool water receives the exogenic precursors such as hair, saliva, urine, body care products, etc. from visitors, which are more reactive than the organic matters from filling water (Kanan and Karanfil, 2011). To date no meaningful relationships between certain compound physiochemical properties and THM formation has been found (Bond et al., 2012). Most studies use sum parameter such as total organic carbon (TOC), dissolved organic carbon (DOC), UV₂₅₄ and/or specific UV absorbance (SUVA) to represent organic precursors. TOC has been proved being able to represent the release of the anthropogenic pollutants (Keuten et al., 2012). In a study of 2 outdoor swimming pools with 81 samples it was estimated that on average 1.09 g DOC per person is brought into swimming pool water (Glauner, 2007). DBP-FP (formation potential) experiments by dosing a certain amount of chlorine are usually applied to elucidate reactive precursors, kinetic behavior and formation mechanisms. Several studies applied body fluid analog (BFA) or materials of human origin to investigate the THM formation yield (Borgmann-Strahsen, 2003; Hansen et al., 2012; Judd and Bullock, 2003). But the BFA might result in a lower THM formation potential due to the fact that the presence of NOM brought by the filling tap water contributes to an additional

DBP formation (Kanan and Karanfil, 2011). In another study urine was added to model solutions containing humic material. The overall THM formation was reduced, which was attributed to the depletion of active free chlorine by forming chloramines (Judd and Jeffrey, 1995). Chlorination experiments of more various materials from human origin mixed within ground water or surface water indicated a significant correlation between TOC and DBP formation but the composition of DBPs can be considerably different due to different water sources (Kim et al., 2002). Experiments with native water rather than only model compounds are needed to have results which are comparable to real situation in the swimming pool.

Many modeling attempts have been made to predict the occurrence of THM in the past three decades but primarily in the field of drinking water. Most of them are function models based on empirical and mechanistic relationships of water quality and operational parameters (Chowdhury et al., 2009). Additionally regression or statistical methods were extensively used (Golfnopoulos and Arhonditsis, 2002). The research of THM modeling has been established in principle by linking THM with water quality parameters including TOC or DOC, type of organic precursors, pH, temperature, reaction time, UV absorbance, chlorine and bromide (Br⁻) concentration, etc. (Abdullah and Hussona, 2013; Sadiq and Rodriguez, 2004). Although the connection of specific model compounds to DBP formation remains uncertain (Hua et al., 2014), generally the increase of chlorine concentration, pH, temperature and reaction time leads to higher formation of THM (Abdullah and Hussona, 2013; Zhang et al., 2013). Some studies tried to establish a proportional relationship between the DBP formation and chlorine consumption. But chlorine consumption may actually largely result from chlorine decomposition or reaction with other reductive substances so that leads to an overestimation (Bond et al., 2012). Moreover, typically the THM lose due to adsorption or volatilization was not considered in these studies on drinking water.

Compared to drinking water, modeling of DBP in swimming pool water attracted much less attention, although that swimming pool has a great recreational value. A possible reason can be the increased complexity of swimming pool water in comparison to the typical drinking water systems due to unpredictable input from visitors, variability and interactions of different precursors and much longer contact time with disinfectant (Chowdhury et al., 2014; Zwiener et al., 2007). Water temperature is typically adapted to the specific requirements with respect to energy or economic aspects and is often set to be certain value in swimming pool. The pH-value is usually kept relatively stable for sufficient chlorination efficiency. However, due to the fact that the bather and contaminant load, chlorine dosage, DBP concentration and fresh filling water can vary considerably both over short and longer time scales, different pool water scenarios are not easily comparable.

Preparation of model swimming pool water in the laboratory is even more difficult. For the less reactive moieties, reactions with chlorine can be too slow to be observed during the drinking water disinfection. Glaumer et al. (2004) observed in an outdoor swimming pool that a THM peak appeared two days after DOC increased. Additionally, effects of such recirculation rates of pool water system on DBPs are not well-understood to date. A few models for THM in indoor swimming pool air have been developed for exposure to THM for visitors (Chen et al., 2011; Hsu et al., 2009). To our knowledge, no simulation to predict THM in swimming pool water was to date established.

The objective of this work is to investigate the occurrence of THM in indoor swimming pool water in correlation with: a) DOC-concentration, b) the number of visitors and c) water treatment process, in order to develop a DOC-based predictive model for THM. Data were acquired through on-site investigations as well as lab-controlled chlorination experiments of native swimming pool water. The results of this study can be used to quantitatively evaluate the THM-formation in swimming pool water.

2. Material and methods

2.1. Tested swimming pool and sampling strategy

Water samples, operational data such as visitor numbers and fresh water consumption for this study were collected at a public indoor swimming pool, which consists of a standard-sized multi-purpose pool (volume 741 m³, surface area 312 m², recirculation flow 95 m³/h) and a smaller wading pool (volume 76 m³, surface area 100 m², recirculation flow 40 m³/h). Both pools are continuously recirculated and treated in parallel by the same water treatment facility with a volumetric flow of 135 m³/h (turnover rate 6 h). The treated water returns to the pool through 4 horizontal line-shape supply devices evenly distributed on the pool bottom (25 m along the length of the pool, distance between each 2.34 m). The treatment process consists of an inline flocculation, powdered activated carbon (PAC) dosage and ultrafiltration (UF), which corresponds to the German industrial norm DIN 19643-4 (DIN, 2012b) describing combination of treatment processes with UF. Dosage of PAC is approx. 1 g/m³, which is 0.135 kg for one treatment passage. The backwash wastewater of UF is treated by a combination of UF-RO and recirculated to the main stream, contributing approx. to 1% of total treatment flow. Disinfection is performed using chlorine gas after UF before water is returned into the pool. The pH-value is controlled by addition of sulfuric acid. A simplified schematic of the pool water system and treatment is shown in Fig. 1. The study site is a typical public swimming pool subjected to a moderate usage mainly by the local residents, averaging around 200 visitors per day including school pupils' classes in the morning on weekdays for approximately 1.5–3 h. Intensive visits from a swimming club of around 100 people came every Friday night.

Water samples were collected regularly in short time intervals. Most samples for month-profile were sampled between 17 and 18 o'clock in the afternoon. Sampling consists of collecting water in the same place in both pools approximately 50 cm from the pool edge and 20 cm under the water surface. The water quality was almost the same at different sampling places. This has been proved by sampling at the four corners, middle and two edges of the pool. Free chlorine, total chlorine, pH-value and temperature were measured daily onsite. Additionally samples were taken in different corresponding glass bottles and transported to the laboratory for the following physical-chemical analysis: DOC, THM, electrical conductivity and ions such as chloride and bromide. Samples were stored at T = 4 °C before measurement and were measured latest within a week. Selected parameters during this period of time are presented in Table 1.

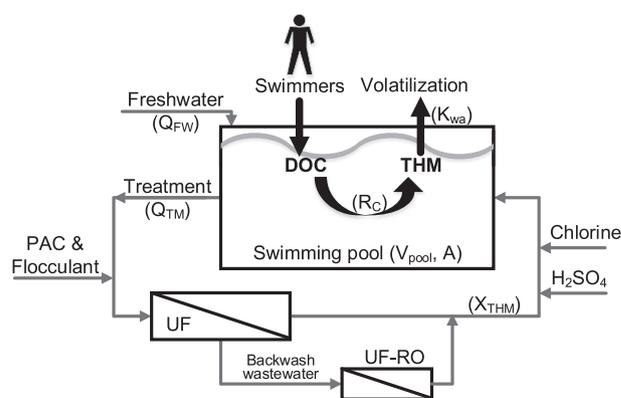


Fig. 1. Simplified schematic of the swimming pool and the treatment process. Q_{FW} is the filling water inflow. Q_{TM} is the volumetric flow rate of pool water treatment (135 m³/h). R_C is the specific ratio representing the production of THM from certain amount of DOC through chlorination. K_{wa} is the overall mass transfer coefficient of THM from water into air. V_{pool} is the total water volume in the swimming pool (817 m³). A is the water surface area of swimming pool (412 m²). X_{THM} is the THM removal ratio in percentage during one passage of the pool water treatment process.

2.2. Analytical methods

Electrical conductivity and pH were measured using a WTW multi set 350i (electrode TetraCon®325 and SenTix 41). DOC was measured using a combustion catalytic oxidation method (Shimadzu Total Carbon Analyzer). The limit of detection was 0.2 mg/L. THM samples were collected in duplicates in 40-mL glass vials and were capped with polytetrafluoroethylene (PTFE)-faced silica septum. Sodium thiosulfate was added to quench the residual free chlorine according to the German DIN-Norm 38407-30 (DIN, 2007). Sampling vials were carefully filled and sealed without air bubbles (headspace free). The determination of THM was carried out using a headspace sampling capillary gas chromatograph (Agilent HP 6890, column DB-5MS) with electron capture detection with purge- and trap-process. The limit of detection were set to 0.4 µg/L for chloroform, 0.2 µg/L for bromodichloromethane, 0.5 µg/L for dibromochloromethane and 0.7 µg/L for bromoform. Each sample was measured at least twice. Anions were measured by ion chromatography (Metrohm IC 790, column Metrosep Anion Dual 3 – 100/4.0). Free chlorine was determined using a photometric-test (Dipropyl-p-phenyldiamine, DPD method, photometer WTW photoLab S12) based on colorimetric method (Spectroquant® cell test Nr. 100597). Applicable range was 0.03–6.00 mg/L free chlorine.

The rest maximum formation potential of THM (THMFP) was measured to analyze to what extent new THM can be formed from the investigated pool water. The method used in this study is according to DVGW-Worksheet standard W 295 (DVGW, 1997). Each test was carried out at least in duplicates. Samples of swimming pool water were taken freshly in 1-L brown reagent bottles full to

Table 1
Physical and chemical parameters of swimming pool and filling water during the period of the study.

Parameter	Unit	Swimming pool water (n = 26)		Filling water (n = 14)	
		Mean ± SD	Range	Mean ± SD	Range
pH		7.1 ± 0.1	6.9–7.5	7.6 ± 0.2	7.6–7.8
Br ⁻	mg/L	<0.1	<0.1	<0.1	<0.3
Cl ⁻	mg/L	66 ± 14	40–86	31 ± 1	29–33
Free chlorine	mg/L	0.4 ± 0.1	0.3–0.6	<0.1	<0.1
DOC	mg/L	3.3 ± 0.3	2.9–4.2	2.7 ± 0.2	2.2–3.0
Temperature	°C	29.4 ± 0.3	28.7–29.6	n. d.	n. d.

n. d.: not determined, SD: standard deviation of the sampling distribution.

the brim, which were made free of chlorine consumption before sampling. In each bottle 20 ± 0.3 mg/L free chlorine was dosed using sodium hypochlorite (12%, Roth, Germany). The same volume of water as the dosage of sodium hypochlorite was taken out before dosing to make the bottle headspace free. After 46 ± 2 h at ambient temperature (21 ± 1 °C) a minimum chlorine residual of 1 mg/L was confirmed and the reaction was stopped by adding an over-stoichiometric amount (one spatula, approx. 0.3 g) of sodium thiosulfate (Merck, Germany), followed by the quantification of THM. The rest maximum THMFP corresponds to the difference of THM concentration before and after the THMFP test.

3. THM simulation

A simple mathematical model for predicting the THM concentration in indoor swimming pool water was proposed based on mass balance. The whole recirculation system of swimming pool water and its treatment process were considered. Water in the swimming pool was assumed to be completely mixed so that THM should be evenly distributed in the pool.

3.1. Formation and removal of THM

The change of THM concentration with time ($d\rho_{\text{THM}}/dt$) is driven by THM formation and removal. DOC was taken as a surrogate for precursors of DBP. THM formation was considered exclusively from the reaction of DOC with chlorine as a first order reaction and assumed to be stoichiometrically proportional to DOC reacted with chlorine. The specific ratio R_C ($\mu\text{g THM}/\text{mg C}$) was introduced, representing the specific production of THM from certain amount of DOC through chlorination:

$$m_{\text{THM}} = R_C \cdot m_{\text{DOC}} \quad (1)$$

whereas m_{THM} is the mass of THM in μg and m_{DOC} is the mass of DOC in mg. Removal of THM from swimming pool water can occur in various ways. For the THM simulation 3 different removal paths were considered: a) volatilization into air, b) exchange of fresh filling water, and c) removal by pool water treatment.

3.2. Volatilization

THM are volatile and have a relatively high Henry's law constant (CHCl_3 : $3.67 \cdot 10^{-3}$ atm m^3/mol ; CHBrCl_2 : $1.60 \cdot 10^{-3}$ atm m^3/mol ; CHBr_2Cl : $7.83 \cdot 10^{-4}$ atm m^3/mol ; CHBr_3 : $5.35 \cdot 10^{-4}$ atm m^3/mol). In swimming pools with traditional treatment process such as flocculation and sand filtration the removal of THM by treatment facility is rather little. The predominant THM removal is due to volatilization into air. Significant linear correlations of THM concentration in pool water and in indoor air were observed by Lourencetti et al. (2012), who indicated a continued transfer of waterborne THM into air. Hsu et al. (2009) observed a gradient of the THM concentration in the air along the height above water surface when there was no visitor in water, while there was no difference in the chloroform concentration in the air for 20–250 cm above water surface when there was any visitor in water. Ventilation is required for indoor swimming pools. Lourencetti et al. (2012) witnessed much lower concentration of THM than the value calculated through Henry's law based on equilibrium. This is probably due to ventilation system in the swimming pool. In this case mass transfer dominates the kinetic THM exchange between water and air in indoor swimming pools. The mass transfer coefficient is a diffusion rate constant to quantify the interphase mass transfer e.g. between water and air in this case. The basic mass transfer equation is:

Mass transfer rate (M/T) = K (L/T) interfacial area (L^2) driving force (M/L^3)

Mass transfer rate is commonly in g/s or mol/s. The driving force here is the concentration difference between two phases; units are g/L or mol/L. K is a proportionality factor called mass transfer coefficient usually in m/s or m/d. Based on two-film theory, the overall mass transfer coefficient considers phase boundary – air and water phase – and can be calculated from Henry's law constant (H_C) and mass transfer coefficient in single phases (Rousseau, 1987). The overall mass transfer coefficient in the liquid phase K_w (m/d) and air phase K_a (m/d) are expressed as:

$$\frac{1}{K_w} = \frac{1}{k_w} + \frac{1}{k_a \cdot H_C} \quad (2)$$

$$\frac{1}{K_a} = \frac{H_C}{k_w} + \frac{1}{k_a} \quad (3)$$

k_w (m/d) is the water-phase mass transfer coefficient and k_a (m/d) is the air-phase mass transfer coefficient. For low-solubility gases such as THM the Henry's constant (H_C) is high. And typically k_a is considerably higher than k_w , which makes K_w the preferred overall coefficient. Under these conditions, the resistance to interfacial mass transfer of THM is liquid-phase controlled (Rousseau, 1987; Tan, 2014). The overall water–air mass transfer coefficient K_{wa} (m/d) is considered equal to K_w in this study. The dimensionless Henry's constant (H_C) for the average water temperature 29.4 °C was calculated according to the method proposed by Sander (1999).

3.3. Treatment

THM removal can be achieved by advanced pool water treatment such as application of activated carbon.

3.4. Exchange of fresh filling water

To keep a certain water volume in swimming pool, water loss due to back-washing of filtration facility, vaporization and bather activities is reflected in the amount of fresh filling water, which should be at least 0.03 m^3 per swimmer according to DIN 19643-1 (2012a). In general tap water is used for filling the pool, where much frequently there is little THM. This exchange with fresh filling water reduces the THM concentration in pool water, which is also occasionally applied in practice to achieve a better water quality. In Germany the drinking water treatment often doesn't apply chlorine. Therefore tap water commonly doesn't contain or contain very little THM. Tap water at the studied swimming pool has THM <0.4 $\mu\text{g}/\text{L}$. Therefore in this study the addition of filling water was considered to cause a reduction on THM concentration.

3.5. Mass balance

In summary, removal of THM from swimming pool water includes: volatilization into air, removal by pool water treatment and exchange with fresh filling water, which can be described by a removal coefficient k (d^{-1}):

$$k = (K_{wa} \cdot A + X_{\text{THM}} \cdot Q_{\text{TM}} + Q_{\text{FW}}) / V_{\text{Pool}} \quad (4)$$

K_{wa} (m/d) is the overall mass transfer coefficient of THM from water into air. A (m^2) is the water surface area of swimming pool. X_{THM} describes the THM removal ratio (in percentage) during one passage of the pool water treatment process. Q_{TM} (m^3/d) is the volumetric flow rate of pool water treatment. Q_{FW} (m^3/d) is the filling water inflow. V_{Pool} (m^3) is the total water volume in the

swimming pool. Based on equation (1) and using k from equation (4) a simple relation based on mass balance of THM in swimming pool water can be expressed as:

$$\frac{d\rho_{\text{THM}}(t)}{dt} = R_C \cdot \rho_{\text{DOC}} - k \cdot \rho_{\text{THM}}(t) \quad (5)$$

ρ_{DOC} (mg/L) and ρ_{THM} ($\mu\text{g/L}$) are the DOC and THM concentrations in pool water. The first part $R_C \cdot \rho_{\text{DOC}}$ represents the THM production and the second part $k \cdot \rho_{\text{THM}}(t)$ stands for THM removal. The parameters for the simulation are integrated in the schematic of the pool water system presented in Fig. 1. Temperature, chlorine concentration and pH-value were assumed to be constant to simplify the simulation as they are usually very stable in indoor swimming pool water. The values of simulation parameters were obtained by our field research and experimental results (Section 4.2). Simulation results were evaluated using the normalized mean bias and mean fractional bias.

4. Results and discussion

4.1. THM and DOC in swimming pool water

To investigate the occurrence of THM and its possible correlation with visitor numbers and other parameters, water quality including DOC, THM and other physical-chemical parameters in an indoor swimming pool were investigated for 26 days. DOC was assumed as precursor to link organic matter and THM formation. The DOC concentration was linked to the number of visitors and THM (Fig. 2). The profiles started on Friday, on which the numbers of daily visitors usually exceeded 330 due to the activity of a swimming club. The DOC concentration in swimming pool water was on average at 3.3 mg/L. On day 12 and day 19 the DOC concentration increased to 3.7 and 4.2 mg/L respectively. The THM concentration varied from 13 to 47 $\mu\text{g/L}$ with an average value of 25 $\mu\text{g/L}$. Alike DOC, we observed two huge peaks of THM at nearly twice of the average concentration, but both came two days after the DOC peaks (day 14 and day 21). The subsequent increases of THM after DOC indicate a clear positive correlation between DOC and THM with a time delay about 2 days. Although this swimming pool has a typical turnover rate of 6 h, increase of DOC showed that the pool water treatment was limited in removing DOC from water. Similar result was reported by Glauner et al. (2004) in an outdoor swimming pool (turnover rate about 4 h). In a weekly profile the maximum concentration of THM followed the increase of DOC after 1–2 day. This kind of

phenomenon is mainly due to the recirculation of pool water, which provides the long reaction time and is not observed in drinking water system. It's likely to conclude that the major THM formation from DOC occurred in the first 48 h during reaction with chlorine. In a chlorination experiment of outdoor swimming pool water Glauner (2007) also pointed out that after 48 h no further increase of THM was observed (chlorine concentration above 2.3 mg/L). Therefore we can speculate that in a conventional swimming pool water treatment the major part of DOC accumulated in pool water and cannot be eliminated by the treatment. Besides, the major part of THM formation in a swimming pool with conventional water treatment takes about 2 days. The time delay should depend on the properties of DOC in water and the treatment, which can be different in the swimming pools with advanced treatment process. Zwiener et al. (2007) also pointed out that this kind of time delay is linked with the treatment cycles needed for efficient chlorination.

We noticed that peaks of THM decreased quickly on the next day when the numbers of visitors were high. A reasonable explanation is the enhanced loss of THM into air due to vigorous activities of the swimmers. Kristensen et al. (2010) has also observed by online monitoring that THMs increased during the closing hours and decrease during opening hours. This implies that the elimination of THMs from pool water correlates strongly with activity in the water, which assists the transfer of THMs from the water into the air by splashing.

Interestingly, the much more intensive visits on Friday didn't have significant effects on DOC value. No direct correlation was observed between DOC and the number of visitors, which is unlike some previous research (Chu and Nieuwenhuijsen, 2002; Glauner et al., 2004). A possible explanation is that the type and amount of input from visitors into swimming pool water depends significantly on their behavior, which might be characterized by different groups (e.g. children or adults, athletes or recreational swimmer, disciplined or incorrect hygienic behavior, etc.). An anonymous questionnaire in Italy showed different hygiene-related behaviors: Only 70.9% of visitors take a shower before entering the swimming pool and 13.5% of visitors have urinated at least once in a swimming pool (Pasquarella et al., 2014). Large variation of input from visitors into swimming pool water due to unhygienic behavior was also reported by Keuten et al. (2014). Compared to outdoor swimming pools this variation is greater in indoor swimming pools which receive more diverse visitor behaviors. We can conclude from our results that introduction of anthropogenic pollutants into swimming pool water and consequent DBP formation cannot be predicted simply from the number of visitors. To estimate the actual DBP formation the content of organic matter should be determined through analytic methods.

4.2. Determination of parameters for the THM simulation

Parameters for the THM simulation were determined using data from field research, laboratory analysis and literature. In the studied pool water temperature was kept at 28.7–29.6 °C and pH was most of the time at 7.1 with a range of 6.9–7.5 (Table 1). Therefore it is realistic to assume the temperature, pH-value and chlorine concentration to be constant for simplifying the simulation. DOC concentration was measured daily. THM formation was considered as a first order reaction and assumed to be stoichiometrically proportional to DOC reacting with chlorine. According to the observed time delay between DOC and THM occurrences in this study, THM formation can be assumed to be the product of the specific ratio R_C ($\mu\text{g THM/mg C}$) and DOC concentration from two days before ($\rho_{\text{DOC}, t-2d}$):

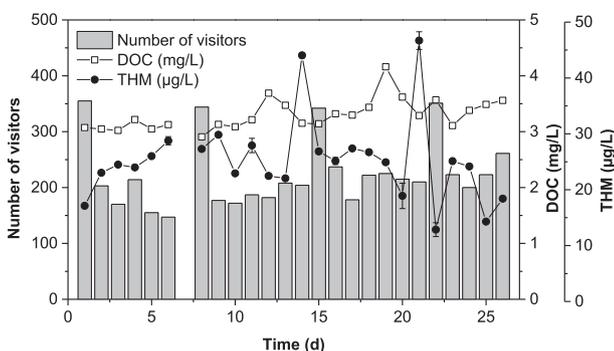


Fig. 2. Profile of the number of visitors, DOC- and THM-concentration obtained from daily sampling for a period of 26 days in the indoor swimming pool water (total water volume 817 m³, water recirculation flow 135 m³/h). Treatment process consists of an inline flocculation, PAC dosage and UF; no PAC was dosed within the first sampling period 16 d.

$$\rho_{\text{THM}}(t) = R_C \cdot \rho_{\text{DOC}, t-2d} \quad (6)$$

The rest maximum formation potential of THM (THMFP) of the native swimming pool water for a reaction time of 46 ± 2 h was determined in the laboratory. R_C was set to the ratio of THMFP/DOC, assuming a maximum THM formation from DOC in two days. THMFP test was carried out 5 times on different days to gain the mean value (23.8 ± 2.4 $\mu\text{g THM/mg C}$). Comparison with data found or calculated from literature shown in Table 2 indicates a good compliance despite the huge variance. In reality, water source, type of organic precursors, pre-oxidation, pre-disinfection or other treatment steps can all affect the DBP species and formation. The steady-state level depends more on the characteristics of the carbon source than on the organic carbon loading rate (Judd and Bullock, 2003). R_C should be always determined using the actual water to be studied.

The mass balance of THM in swimming pool (equation (5)) can be expressed as:

$$\frac{d\rho_{\text{THM}}(t)}{dt} = R_C \cdot \rho_{\text{DOC}, t-2d} - k \cdot \rho_{\text{THM}}(t) \quad (7)$$

After integration, the THM concentration in swimming pool was obtained as:

$$\rho_{\text{THM}}(t) = \left(\rho_{\text{THM},0} - \frac{R_C \cdot \rho_{\text{DOC}, t-2d}}{k} \right) \cdot e^{-k \cdot t} + \frac{R_C \cdot \rho_{\text{DOC}, t-2d}}{k} \quad (8)$$

The measured THM concentration on day 1 was used as $\rho_{\text{THM},0}$ (start value of the simulation). Variables for k ($= (K_{\text{wa}} \cdot A + X_{\text{THM}} \cdot Q_{\text{TM}} + Q_{\text{FW}}) / V_{\text{Pool}}$) were determined separately.

4.3. Volatilization

Typically there are two air exchanges per hour at a fresh air supply of 50% for ventilation in an indoor swimming pool in Germany (Schmalz et al., 2011). In this study a uniform indoor airflow for the whole room was assumed. Frequently chloroform dominates in the total THM (Bessonneau et al., 2011; Simard et al., 2013). In our study we found exclusively chloroform and bromodichloromethane present. Chloroform accounts more than 95% by mass (Table 3). Therefore one general overall mass transfer coefficient K_{wa} is assumed here for the total THM. A general airflow velocity in indoor swimming pool was reported for 0.05–0.35 m/s

Table 3

Single species of THM in the indoor swimming pool water and filling water for the first sampling period of 26 d.

Parameter	Unit	Swimming pool water (n = 26)		Filling water (n = 14)
		Mean \pm SD	Range	
CHCl ₃	$\mu\text{g/L}$	24.2 \pm 7.2	12.3–45.7	<0.4
CHCl ₂ Br	$\mu\text{g/L}$	1.4 \pm 0.3	0.8–2.1	<0.2
CHClBr ₂	$\mu\text{g/L}$	<0.5	<0.5	<0.5
CHBr ₃	$\mu\text{g/L}$	<0.7	<0.7	<0.7

SD: standard deviation of the sampling distribution.

from field survey (Hsu et al., 2009). Based on formulas provided by Guo and Roache (2003) using the airflow velocity of 0.35 m/h and the average water current velocity of 2 m/s in swimming pool (Toussaint and Truijens, 2005), the K_{wa} of chloroform was calculated to be 0.132 m/h. Besides, a K_{wa} value of 0.378 m/h could be calculated by mass transfer coefficients for chloroform in water and air of an indoor swimming pool reported by Dyck et al. (2011). In this study, K_{wa} was set to be 0.237 m/h by fitting the simulated data to the measured THM concentrations. This value is within the range that gained from literature. The removal coefficient k depends mainly on K_{wa} due to the high volatilization rate of THM.

4.4. Treatment

PAC was dosed before UF, which should have a certain effect on removal of THM considered as removal ratio X_{THM} . The dosage of PAC was absent in the first 16 days. By sampling at the inlet and outlet of treatment process no elimination of THM was observed. After the day 17, PAC has been dosed. The elimination of THM by PAC could be distinguished as 1% during one treatment passage. This value was used for simulation as elimination efficiency of THM (X_{THM}) after the day 17. The low elimination rate can be attributed to the short contact time with PAC during the treatment passage, which is only approximately 20 s. It explains also the occurrence of high THM-concentration in the pool water which could not be removed by PAC.

4.5. Exchange of fresh filling water

The amount of daily filling water Q_{FW} was provided by the swimming pool staff, averaging approximately 21 m³/d during our study. In this study exchange with filling water was assumed to

Table 2

Specific THM formation ratio R_C ($\mu\text{g THM/mg C}$) found or calculated from literature.

R_C $\mu\text{g THM/mg C}$	Water source	Temperature $^{\circ}\text{C}$	Initial chlorine mg/L	Reaction time d	Source
33.8	Indoor swimming pool	21	20	2	This study
18.7	Body fluid analog in laboratory	Ambient	20	2	(Glauner, 2007)
35.7–44.9	Tap water	Ambient	20	2	
51	Outdoor swimming pool	Ambient	20	2	(Glauner et al., 2005)
68	Outdoor swimming pool	Ambient	20	2	
19	Groundwater	30	6	3	(Kim et al., 2002)
16.7	Groundwater + material of human origin	30	6	3	
31.7	Surface water	30	6	3	
14.2	Surface water + material of human origin	30	6	3	
16–38	Body fluid analog in laboratory	26	50	5	(Kanan and Karanfil, 2011)
12–307	Body fluid analog in laboratory	22	50	5	
48–106	Filling water before oxidation	26	50	5	

have only removal effect on THM. However, for the locations with tap water containing THM it should be considered in the water exchange.

The comparison of measured and fitted THM concentrations in pool water is shown in Fig. 3. The general level of simulated and measured data fits with each other. The appearance of THM peaks could be predicted on the right day. However, the expressively high concentrations of THM peaks could not be predicted, which may attribute to underestimation of the reactivity of some organic matters with chlorine, probably brought into pool water by pool visitors. The simulation can be improved only if more information about the formation rate between different DOC constituents and THM is gained. Nevertheless, at the end the predicted value on day 28 fit very well with the measured value despite that there was a gap of measurement on day 27.

4.6. Validation of simulation

Validation of model requires assessing the effectiveness of the fitted equation against an independent set of data. To validate the simulation we used the data from further sampling for 50 days. Simulation started with the measured THM concentration on day 2 because of the delay between DOC concentration and THM formation. Comparison between measured and simulated THM concentration are presented in Fig. 4. The simulated and measured THM concentrations were generally in good agreement. The simulated results represented well the tendency of THM accumulation and removal for most of the THM peaks. Slight overestimation appeared on day 27–31 and day 35–36, which may be attributed to the underestimation of the various contributions of visitors' movement to the volatilization. The movement behavior of visitors in swimming pool could strongly affect the volatilization rate of THM into air in indoor swimming pools (Hsu et al., 2009; Kristensen et al., 2010). In addition, the expressively high THM-concentration (>40 µg/L) during the first sampling period (Fig. 3) were not observed in these 50 days (Fig. 4). We may again speculate that the excessive THM-concentration might be a short-term value due to some reactive organic matters. In the later time after day 37 the development tendency of THM was again well approved by the actual measurement. Normalized mean bias (NMB) and mean fractional bias (MFB) were calculated as described by Dyck et al. (2011):

$$\text{Normalized mean bias (\%)} = \frac{\sum_{i=1}^N (Y_{\text{predicted}} - Y_{\text{measured}})}{\sum_{i=1}^N Y_{\text{measured}}} \cdot 100 \quad (9)$$

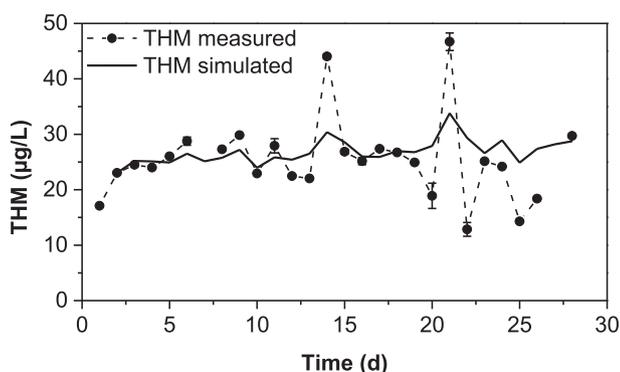


Fig. 3. Measured and fitted THM concentrations in the indoor swimming pool water for the first sampling period.

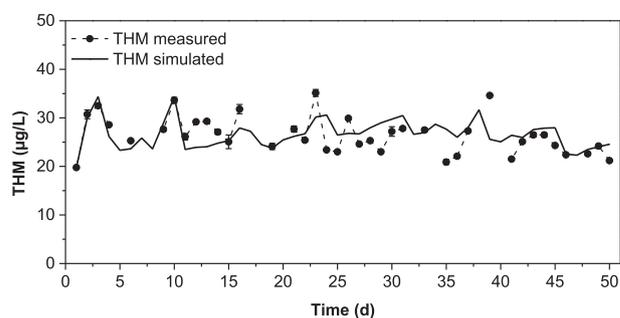


Fig. 4. Validation for measured and simulated THM concentrations in the indoor swimming pool water for a further period of 50 d.

$$\text{Mean fractional bias (\%)} = \frac{1}{N} \sum_{i=1}^N \frac{2 \cdot (Y_{\text{predicted}} - Y_{\text{measured}})}{(Y_{\text{predicted}} + Y_{\text{measured}})} \cdot 100 \quad (10)$$

The NMB and MFB of predicted THM were 1.6% and 1.5%, which presented a close simulation. The validated simulation confirms that DOC concentration has a dominant effect on THM concentration in swimming pool water after two days. A sensitivity analysis was performed for the key parameters R_C and K_{wa} for the second period of 50 days (Supporting information, Fig. S1). The sensitivity analysis indicates that increase and decrease of R_C has a linear effect on the simulation. K_{wa} is more sensitive for lower values and tends to overestimate the THM concentration. When the decrease of K_{wa} is bigger than -30% , the overestimation of THM increases significantly. Increase of K_{wa} has a lower impact and tends to be less sensitive when the change is higher than 30% .

A simulation of THM in swimming pool water by the use of kinetic coefficient relating them to actual water quality and operational parameters was established. Formation ratio R_C of THM gained in laboratory analysis using native pool water and field sampling for relating the coefficients to operational parameters reduced the uncertainty of prediction. Establishing the formation ratio improves our understanding of the role of DOC in the THM formation which can help to manage DBP precursors in source and pool water. The unknown various activities of pool visitors and different type of organic matter are critical for THM simulation. Intensive activities contribute significantly to the volatilization of THM, which leads to an overestimation of THM concentration by the simulation model. The different reactive organic matters brought by visitors are associated with different THM formation potential, which affects also the accuracy of simulated results. It's been indicated that fractions of DOC has various THMFP (Glauner et al., 2005). Therefore determination of R_C should use the native pool water to obtain reliable simulation results. Moreover, recently haloacetic acids (HAA) have gained much attention. The reported HAA concentrations in swimming pool water are much higher than those for THM, possibly because the formation potential of HAA is higher and HAA are much less volatile than THM (Chowdhury et al., 2014). If the pool water treatment is not able to remove HAA and/or their precursors, an accumulation will be probably observed. Due to the much lower volatility the modeling of HAA in swimming pool water could also be feasible using a similar approach based on mass balance.

This simulation model provides a useful method for predicting THM concentration in indoor swimming pool water for a given concrete scenario. With a reduced amount of data required such as a few times of THMFP tests and determination of THM removal by the existing treatment process, formation trend of THM under indoor swimming pool water conditions can be estimated even for

long term. For conventional pool water treatment process the low THM removal rate can be neglected.

5. Conclusions

The formation of THM in swimming pool water showed a clear positive correlation to DOC with a time delay in this study, which is related to the treatment process. For conventional swimming pool treatment process the major part of THM formation is within 2 days. DOC proved to be a suitable parameter for precursor to predict THM production when reaction time of 2 days is considered. Number of visitor is not reliable to estimate the organic load brought into water and to predict THM formation. For the first time we developed a simple simulation based on mass balance for predicting the THM concentration in indoor swimming pool water. The model can be used to estimate THM concentration under real indoor swimming pool water conditions with a reduced amount of data required. In the simulation, production of THM from reaction of DOC and chlorine, lose into air and elimination by pool water treatment were considered. The simulated results were generally in well agreement with measurements in reality and in good compliance with published characteristics. The unknown variance of characteristics of DOC and activities of visitors contributed to the deviation between the measurement and the simulation. Practically the model can be useful in conducting health-related risk assessment concerning exposure to DBP and in estimating infrastructure needs for upgrading treatment facilities. The production of THM from DOC is slow compared to a typical turnover rate of swimming pool water. Therefore, a quick removal of organic precursors through pool water treatment could be an effective way to minimize the THM production.

Acknowledgment

The authors thank the German Federal Environmental Foundation (DBU) for the financial support (Az: 28707-23), the DVGW-Research Center, the W.E.T. GmbH and the co-workers in the studied swimming pool for the collaboration, Elly Karle, Axel Heidt and Matthias Weber for the technical support in laboratory work.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2015.10.061>.

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