

Health Risk Assessment of Trihalogenmethanes in Drinking Water

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Abstract—Trihalogenmethanes (THMs) are disinfection byproducts with non-carcinogenic and genotoxic effects. The contamination of 6 sites close to the water treatment plant has been monitored in second largest city of the Czech Republic. Health risk assessment including both non-carcinogenic and genotoxic risk for long term exposition was realized using the critical concentrations. Concentrations of trihalogenmethanes met national standards in all samples. Risk assessment proved that health risks from trihalogenmethanes are acceptable on each site.

Keywords—Drinking water, health risk assessment, trihalogenmethanes, water pollution.

I. INTRODUCTION

WATER intended for human consumption is called drinking water and is defined in national legislation [1] and international directive too [2]. Not all water is suitable for treatment in order to obtain drinking water. According to the composition of the source water are correct methods and their combination of the water treatment chosen. In general filtration and disinfection are always used [3].

The purpose of disinfection is to ensure bacteriological safety and prevent the spread of the infectious diseases. Disinfection is one of the last steps in the water treatment process [3]. Nowadays is chlorine, chlorine dioxide, chloramines, ozone or ultraviolet disinfection used. Combination of the chlorination and ozone disinfection is worldwide extended [4]. There is a tendency to use UV disinfection because of its indisputable advantages. Both of these methods are highly effective against resistant pathogens like cryptosporidium [5].

A number of products called disinfection byproducts (DBPs) are formed during the disinfection process. Their quantity depends on disinfection method, chemical and physical properties of water. During ozone and UV disinfection are produced the lowest concentration of the DBPs [6].

II. ANALYSIS OF CURRENT STATE

Among the DBPs which occur in the highest concentrations and have the potential to seriously threaten the health of consumers belong chloroform (CHCl_3), bromdichlormethane (CHBrCl_2), dibromchlomethane (CHBr_2Cl), and bromoform

(CHBr_3). Mentioned pollutants fall among trihalogenmethanes (THMs) [4].

International levels for THMS pollution vary between 25-250 $\mu\text{g dm}^{-3}$ according to the World Health Organization (WHO) [7]. Limit of total amount of THMs in drinking water was reduced from 150 to 100 $\mu\text{g dm}^{-3}$ in the Czech Republic in 2010 and correspond to the European Union requirement [2]. US Environmental Protection agency (US EPA) sets maximum contamination level for THMs as 80 $\mu\text{g dm}^{-3}$ [8].

Attention is not only given to the total amount of THMs but also to the concentrations of the individual pollutants. Czech Republic has THMS amount allowable concentration higher than the USEPA; however, limits for chloroform are lower than those provided for US EPA and WHO. WHO does not, unlike the standards of the above mentioned institutions, specific limits for each pollutant, but pays attention only the summation content THMs [9].

The reaction rate and the spectrum of created DPBs depends on the water temperature and pH [10], on the content of ions Mo^{2+} , Na^+ , K^+ , Fe^{2+} , Mn^{2+} and Ca^{2+} [11], the type and dose of applied disinfection agent, concentration and chemical composition of the organic precursors in the water and distribution system and the time that water remains in disinfection [12], [13]. Authors disagree on what proportion has THMs on the total amount of DPBs [14]. The major pollutant is chloroform [6].

THMs enter to the human body through three exposure pathways—ingestion, inhalation and dermal contact. They have neurotoxic, immunotoxic, cytotoxic, hepatotoxic and nephrotoxic effects [15], [16]. Carcinogenic, mutagenic, teratogenic and embryotoxic effects are not excluded [16]. There are suspicions that higher concentrations of bromdichlormethane causes spontaneous abortions, reduced birth weight, and increase in the risk of defects, although this fact was not sufficiently demonstrated [17].

Bromoform, chloroform, dibromchlormethane and bromdichlormethane are volatile colorless to yellowish liquid, odorless or with slightly sweet odor [18]-[21]. Tests on animals have shown genotoxic effects of chloroform [22], dibromchlormethane [9], bromdichlormethane [23] and bromoform [24]. US EPA classified chloroform into B2 group same as bromoform [25], [26] and bromdichlormethane into group C [9].

III. APPLIED METHODS AND DEVICES

The samples of drinking water have been taken and analyzed according to the relevant standards [27]. The concentration of THMs in the samples of drinking water has

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been determined by the liquid-gas extraction technology with the help of the TriPlus static head space dosing device and the Trace GC Ultra gas chromatograph with the Trace DSQ mass detector, produced by Thermoelectron Corporation. The limit of determination for individual THMs was 0.1 or 0.5 $\mu\text{g dm}^{-3}$.

The assessment of health risks was carried out in compliance with the valid Czech guidelines and instructions [28], which are based on the method proposed by the U.S. EPA [29].

The hazard quotient HQ characterizes non-carcinogenic risks as the ratio of the exposure dose expressed as CDI and the reference dose RfD according to (1):

$$HQ = CDI \times RfD^{-1} \quad (1)$$

where CDI [$\mu\text{gkg}^{-1}\text{day}^{-1}$] represents chronic daily intake and RfD [$\mu\text{gkg}^{-1}\text{day}^{-1}$] reference dose.

Chronic daily intake has been calculated for each exposure pathway according to relations (2), (3) and (4) when ING means ingestion, DC dermal contact and INH inhalation.

$$CDI_{ING} = c_w \times IR_{ING} \times b \times EF \times ED \times BW^{-1} \times AT^{-1} \quad (2)$$

$$CDI_{DC} = c_w \times SA \times K_p \times ET \times EF \times ED \times C_F \times BW^{-1} \times AT^{-1} \quad (3)$$

$$CDI_{INH} = c_a \times IR_{INH} \times ET \times EF \times ED \times BW^{-1} \times AT^{-1} \quad (4)$$

where c_w [$\mu\text{g dm}^{-3}$] is the concentration of contaminant in drinking water acquired through measurement, IR_{ING} [$\text{dm}^3 \text{day}^{-1}$] is the daily rate of consumed water, b the rate of consumed water from private sources, EF [days] is the exposure frequency, SA [cm^2] the skin area which is in contact with contaminated water, K_p [cm hour^{-1}] the coefficient of skin permeability, CF is the cm^3 to dm^3 conversion factor, c_a [$\mu\text{g m}^{-3}$] the concentration of contaminant in air calculated according to (5), IR_{INH} [$\text{m}^3 \text{hour}^{-1}$] the rate of air inhaled per

hour, EF [days week⁻¹] the annual exposure frequency, ET [hour day⁻¹] the daily exposure time, ED [years] the exposure duration, BW [kg] the average body weight and AT [day] is the time during which the concentration c_w of contaminant may be considered constant.

$$c_a = c_w \times f \times Q \times t \times V^{-1} \times 2^{-1} \quad (5)$$

where f represents the fraction of releasable contaminant, Q [$\text{dm}^3 \text{hour}^{-1}$] the water flow per hour, t [hour] the showering time, and finally V [m^3] is the volume of bathroom.

When $HQ \leq 1$ the risk is acceptable, in case $1 \leq HQ < 4$ risk is tolerable and when $HQ > 4$ the risk is unacceptable.

The acceptability of genotoxic risk is given by excess lifetime cancer risk $ELCR$ value. This can be calculated from the chronic daily intake CDI , which is same as CDI in case of the non-carcinogenic risks, and the known cancer slope factor CSF [$\text{kg day } \mu\text{g}^{-1}$] for individual exposure pathways according to the relation (6):

$$ELCR = 1 - e^{-(CSF \times CDI)} \quad (6)$$

The acceptable limit for the socially genotoxic risk is $ELCR \leq 10^{-4}$.

Associated uncertainty related to errors in measurements and estimation of exposure factors.

IV. OUTCOMES AND DISCUSSION

Sampling has been carried out in Brno which is the second largest city of the Czech Republic. There have been 6 locations near the water treatment plant, where the disinfection with gaseous chlorine takes place. Table I shows the averages concentrations of THMs in individual sites. The number of measurements in each site ranged from 3 to 7.

TABLE I
THE CONCENTRATIONS OF THMS

Average concentration of contaminants [$\mu\text{g dm}^{-3}$]	Site					
	1	2	3	4	5	6
CHCl_3	1.433	2.02	0.386	0.543	0.597	0.627
CHBrCl_2	2.066	1.840	0.342	0.386	0.321	0.586
CHBr_2Cl	2.330	1.780	0.329	0.329	0.300	0.386
CHBr_3	0.533	0.880	0.514	0.514	0.586	0.657

The chronic daily intake was calculated for long-term residents using the following exposure factors: the daily water intake IR_{ING} was set as $1.4 \text{ dm}^3 \text{ day}^{-1}$, the consumed water from private sources b as 1, the rate of air inhaled per hour IR_{INH} $0.6 \text{ m}^3 \text{ hour}^{-1}$, the fraction of releasable contaminant f was 0.75, the water flow per hour Q as $600 \text{ dm}^3 \text{ hour}^{-1}$, the showering time t was 0.33 hour, V is the volume of bathroom and was set as 9 m^3 , the skin area which is in contact with contaminated water SA was 18000 cm^2 , K_p the coefficient of skin permeability $0.01 \text{ cm hour}^{-1}$, $CF = 10^{-3} \text{ dm}^3 \text{ cm}^{-3}$. In the case of the inhalation and the dermal contact were the daily exposure time ET $0.33 \text{ hour day}^{-1}$. The body weight BW was

70 kg , the exposure duration ED 70 years, the exposure frequency EF was 350 days and finally the time during which the concentration c_w of contaminant may be considered constant AT was 25550 days for all expositions.

Concentration of THMs in all samples met maximum allowed concentration according to the national legislation same as the international recommendation. Pollutant which was observed in the highest levels was chloroform. Contrary the lowest concentrations were found in the case of dibromochloromethane.

The reference doses RfD are in Table II and the cancer slope factors CSF for each contaminants and exposure ways are in

Table III [16], [30]. According to (2)-(4) chronic daily intakes were calculated. Results are shown in Table IV.

TABLE II
VALUES OF REFERENCE DOSES FOR PARTICULAR THMS AND EXPOSURE WAYS

Reference dose	Unit	CHCl ₃	CHBrCl ₂	CHBr ₂ Cl	CHBr ₃
Ingestion RfD_{ING}	$\mu\text{g kg}^{-1} \text{den}^{-1}$	10.0	20.0	20.0	20.0
Inhalation RfD_{INH}	$\mu\text{g kg}^{-1} \text{den}^{-1}$	8.6E-02	-	-	-
Dermal contact RfD_{DC}	$\mu\text{g kg}^{-1} \text{den}^{-1}$	2.0	-	-	-

TABLE III
VALUES OF CANCER SLOPE FACTORS FOR PARTICULAR THMS AND EXPOSURE WAYS

Exposure pathway	Unit	CHCl ₃	CHBrCl ₂	CHBr ₂ Cl	CHBr ₃
Ingestion CSF_{ING}	$\text{kg day } \mu\text{g}^{-1}$	6.1E-06	6.2E-05	8.4E-05	7.9E-06
Inhalation CSF_{INH}	$\text{kg day } \mu\text{g}^{-1}$	8.1E-05	-	-	3.9E-06
Dermal contact CSF_{DC}	$\text{kg day } \mu\text{g}^{-1}$	3.1E-05	-	-	-

Under the assumption non carcinogenic risk is acceptable when $HQ \leq 1$ and using appropriate reference dose RfD the critical concentration has been deduced from (1) using (2)-(4) for each exposure pathway. The calculated critical concentrations for non-carcinogenic risk c_{nc} are shown in

Table IV. Analogously the critical concentrations in relation to genotoxic risk have been calculated according to (6) and cancer slope factors CSF when $ELCR = 10^{-4}$. Critical concentrations for genotoxic c_g risks are in Table V.

TABLE IV
CRITICAL CONCENTRATION C_{NC} FOR NON-CARCINOGENIC RISK

Exposure pathway	Unit	CHCl ₃	CHBrCl ₂	CHBr ₂ Cl	CHBr ₃
Ingestion	μg	521.429	1042.857	1042.857	1042.857
Inhalation	μg	3.843	-	-	-
Dermal Contact	μg	2457.912	-	-	-

It is clear from Tables IV and V that observed concentrations are multiply lower than calculated critical concentration. The lowest observed critical concentration are for chloroform and inhalation exposure way. In this case is the critical concentration for non-carcinogenic risk only three

times higher. Negative effects of chloroform are well known and described in the literature. It is therefore possible to assume that chloroform is also in Brno, the most important pollutant from the group THMS.

TABLE V
CRITICAL CONCENTRATION C_g FOR GENOTOXIC RISK

Exposure pathway	Unit	CHCl ₃	CHBrCl ₂	CHBr ₂ Cl	CHBr ₃
Ingestion	μg	854.801	84.101	62.075	660.036
Inhalation	μg	55.172	-	-	1145.880
Dermal Contact	μg	3964.375	-	-	-

It is possible that at sites closer to disinfection point where are the concentrations highest [31] inhabitants could feel some effects results from exposition to THMS, for example headache or dizziness. These are caused not only by exposure to THMs but also increased the temperature and humidity in unventilated bathroom.

V. CONCLUSION

Trihalogenmethanes are pollutants with variety of negative effects on human health including both non-carcinogenic and genotoxic risk.

Critical concentrations based on health risk assessment are not only useful for risk assess but also provide a clear overview about how they differ from those observed concentrations that represent the limits of acceptability or tolerability of health risk.

Health risk assessment using comparison of observed concentration and calculated critical concentration proved that water pollution in Brno city is on acceptable level. The main pollutant which observed concentrations are the closest to the critical concentration is chloroform.

The authors believe that a well-ventilated bathrooms ensure low concentrations THMS in air and ensure adequate protection of the population at the surveyed sites.

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