

# Health Risk Assessment of Trihalogenmethanes in Drinking Water

Lenka Jesonkova, Frantisek Bozek

**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 ( $\text{CHCl}_3$ ), bromdichlormethane ( $\text{CHBrCl}_2$ ), dibromchlomethane ( $\text{CHBr}_2\text{Cl}$ ), and bromoform

( $\text{CHBr}_3$ ). 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  $\text{Mo}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Ca}^{2+}$  [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 bromdichlormethan 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

Lenka Jesonkova is with the Civil Protection Department, University of Defence, Brno, Kounicova 65, 662 10, Czech Republic (phone: 00420973442097; e-mail: lenka.jesonkova@unob.cz).

Frantisek Bozek is with the Civil Protection Department, University of Defence, Brno, Kounicova 65, 662 10, Czech Republic (phone: 00420973443170; e-mail: frantisek.bozek@unob.cz).

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,  $SA$  [ $\text{cm}^2$ ] the skin area which is in contact with contaminated water,  $K_p$  [ $\text{cm hour}^{-1}$ ] the coefficient of skin permeability,  $CF$  is the  $\text{cm}^3$  to  $\text{dm}^3$  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  $V$  [ $\text{m}^3$ ] 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
$\text{CHCl}_3$	1.433	2.02	0.386	0.543	0.597	0.627
$\text{CHBrCl}_2$	2.066	1.840	0.342	0.386	0.321	0.586
$\text{CHBr}_2\text{Cl}$	2.330	1.780	0.329	0.329	0.300	0.386
$\text{CHBr}_3$	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  $9 \text{ m}^3$ , the skin area which is in contact with contaminated water  $SA$  was  $18000 \text{ cm}^2$ ,  $K_p$  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

$70 \text{ kg}$ , 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 <sub>3</sub>	CHBrCl <sub>2</sub>	CHBr <sub>2</sub> Cl	CHBr <sub>3</sub>
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 <sub>3</sub>	CHBrCl <sub>2</sub>	CHBr <sub>2</sub> Cl	CHBr <sub>3</sub>
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 <sub>3</sub>	CHBrCl <sub>2</sub>	CHBr <sub>2</sub> Cl	CHBr <sub>3</sub>
Ingestion	$\mu\text{g}$	521.429	1042.857	1042.857	1042.857
Inhalation	$\mu\text{g}$	3.843	-	-	-
Dermal Contact	$\mu\text{g}$	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 <sub>3</sub>	CHBrCl <sub>2</sub>	CHBr <sub>2</sub> Cl	CHBr <sub>3</sub>
Ingestion	$\mu\text{g}$	854.801	84.101	62.075	660.036
Inhalation	$\mu\text{g}$	55.172	-	-	1145.880
Dermal Contact	$\mu\text{g}$	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.

## REFERENCES

- [1] G. O. Ministry of Health of the Czech Republic (MoHCR). Decree No. 258/2000 Coll., The protection of public health. Prague, 2000.
- [2] The Council of the European Union. (CEU). Council Directive 98/83/EC on the Quality of Water Intended for Human Consumption. Brussels: CEU, 1998.
- [3] Pitter, P.: Hydrochemie. Vydavatelství VŠCHT Praha, Praha 2009.
- [4] Bozek, F., Bozek, M., Dvorak, J. Trihalogenmethanes in Drinking Water and Quantification of Health Risks. WSEAS Transactions on Environment and Development, 2011, 7, (4), pp. 103-113.

- [5] Kozisek, F, Pumann, P. Infectious diseases from drinking water. The National Institute of Public Health. [online].2008 [cit. 2013-01-10]. URL:<http://www.szu.cz/tema/prevence/infekcni-onemocneni-z-pitne-vody>.
- [6] Singer, P. C. Control of Disinfection By-Products in Drinking Water. *Journal of Environmental Engineering*, 1994, 120,(4), 727-744.
- [7] WHO. Guidelines for Drinking-Water Quality.Vol. 1 Recommendations. 1st Addendum to 3rd; Geneva: WHO, 2006.
- [8] U.S.EPA. Drinking Water Contaminants. [online], [cit. 2013-05-18]. URL: <http://water.epa.gov/drink/contaminants/index.cfm>
- [9] WHO. Guidelines for Drinking-water Quality. Vol. 4.. Switzerland: WHO, 2011.
- [10] Sun, Y. et al. Effects of Operating Conditions on THMs and HAAs Formation During Wastewater Chlorination. *Journal of Hazardous Materials*, 2009, 168, (2-3), pp. 1290-1295.
- [11] Liu, X., et al. Effects of Metal Ions on THMs and HAAs Formation During Tannic Acid Chlorination. *Chemical Engineering Journal*, 2012, 211-212, pp. 179-185.
- [12] Hamidin, N. et al. Human Health Risk Assessment of Chlorinated Disinfection By Products in Drinking Water Using a Probabilistic Approach. *Water Research*. 2008, 42, pp. 3263-3274.
- [13] Whitaker, H. et al. Description of Trihalomethane Levels in Three United Kingdom Water Suppliers. *Journal of Exposure Analysis and Environmental Epidemiology*, 2003, 13,(1), pp. 17-23.
- [14] Colman, J. et al. Identification of developmentally toxic drinking water disinfection by products and evaluation of data relevant to mode of action. *Toxicology and Applied Pharmacology*. 2011, 254, 100-126.
- [15] Larson, J. L., Wolf, D. C., Butterworth, B. E. Acute Hepatotoxic and Nephrotoxic Effects of Chloroform in Male F-344 Rats and Female B6C3F1 Mice. *Toxicol. Sci.*, 1993, 20, (3), pp. 302-315.
- [16] U.S. EPA. Integrated Risk Information System (IRIS).Database of Toxicological Parameters for Human Health.[online]. [2010 03 06]. URL: <http://www.epa.gov/iris/subst>.
- [17] Nieuwenhuijsen et al. Chlorination Disinfection Byproducts in Water and Their Association with Adverse Reproductive Outcomes: A Review. *Occupational and Environmental Medicine*, 2000, 57,(2), 73-85.
- [18] U.S. Environmental Protection Agency. Chloroform. 2007. [online], [2013 05 18]. URL: <http://www.epa.gov/ttnatw01/hlthef/chlorofo.html>.
- [19] Agency for Toxic Substances and Disease Registry (ATSDR). Toxicological Profile for Chloroform. Public Health Service, U.S. Department of Health and Human Services, Atlanta, GA. 1997.
- [20] U.S. Environmental Protection Agency. Bromoform. 2007. [online], [2013 05 18]. <http://www.epa.gov/ttnatw01/hlthef/bromofo.html#ref1>.
- [21] Agency for Toxic Substances and Disease Registry (ATSDR). Toxicological Profile for Bromoform and Chlorodibromomethane. Public Health Service, U.S. Department of Health and Human Services, Atlanta, GA. 1990.
- [22] Agency for Toxic Substances and Disease Registry (ATSDR). Toxicological Profile for Bromodichloromethane. Public Health Service, U.S. Department of Health and Human Services, Atlanta, GA. 2011.
- [23] U.S. Environmental Protection Agency. Integrated Risk Information System (IRIS) on Chloroform. National Center for Environmental Assessment, Office of Research and Development, Washington, DC. 1999.
- [24] U.S. Environmental Protection Agency. Integrated Risk Information System (IRIS) on Bromodichloromethane. National Center for Environmental Assessment, Office of Research and Development, Washington, DC. 2012.
- [25] Agency for Toxic Substances and Disease Registry (ATSDR). Toxicological Profile for Bromoform and Chlorodibromomethane. Public Health Service, U.S. Department of Health and Human Services, Atlanta, GA. 1990.
- [26] Agency for Toxic Substances and Disease Registry (ATSDR). Toxicological Profile for Chloroform. Public Health Service, U.S. Department of Health and Human Services, Atlanta, GA. 1997.
- [27] Czech Office for Standards, Metrology and Testing (COSMT). ČSN EN ISO 5667-3. Water Quality-Sampling-Guidance for the Preservation of Samples and Handling. Prague : COSMT, 2004.
- [28] Ministry of Environment (MoE). Metodická Instrukce No 12 for the Risk Analysis of Contaminated Area. MoE Bulletin, Vol XXI, Article 3, 2011, pp. 1-64.
- [29] U.S. EPA. Risk Assessment Guidance for Superfund: Human Health Evaluation Manual. Interim Final. EPA/540/1-89/002, Washington, D.C.: U.S. EPA, 1989.
- [30] U.S. EPA. EPA Superfund, Record of Decision. EPA/ROD/R04 01/534. Washington, D.C.
- [31] Bozek, F., Jesonkova, L., Dvorak, J. Incidence of Trihalogenmethanes in Drinking Water. *World Academy of Science, Engineering and Technology*, (68), 2012, pp. 322-325.