# RISK ASSOCIATED WITH HUMAN EXPOSURE TO TRIHALOMETHANES (THMs) IN THE WATER DISTRIBUTION NETWORK OF CLUJ-NAPOCA

***CORNELIA DIANA ROMAN[1], ANCA ELENA GURZĂU[2], ALEXANDRU ZEIC[2]***

**ABSTRACT – Risk associated with human exposure to trihalomethanes (thms) in the water distribution network of Cluj-Napoca.** Trihalomethanes (THMs), as disinfection by-products resulted from water chlorination, can get into the body through ingestion of beverages, food or drinking water. This paper discusses the relationship between the use of drinking water from the public distribution network of Cluj-Napoca and exposure to trihalomethanes. To better characterize individual water consumption, at home and at work, we applied a questionnaire to a group of 211 subjects from Cluj-Napoca, while assessing their current exposure to THMs by collecting and analyzing water from different points of the distribution network. The data obtained were statistically processed and then used to calculate the exposure dose and cancer risk for both adults and children. The results showed that subjects consumed for drinking both bottled water and water from the distribution network, but for preparing food and beverages (tea, coffee) they used only water from the public distribution network. The average daily consumption of drinking water from the distribution network, is 1.4 l/day for adults, including beverages prepared with treated water. The surveyed subjects declared that they consume coffee or tea, in percentage of 88%, 94.4% respectively. The calculation of the exposure dose, daily intake and risk of cancer was achieved by using a model developed by the Agency for Toxic Substances and Disease Registry (ATSDR) from the USA to calculate the dose and assess the risk of cancer. Our study shows that the cancer risk to THMs is increasing related to the higher daily intake of the drinking water, being higher for chloroform compared to dibromochloroform. For the measured concentrations of chloroform and dibromochloroform in drinking water and the average daily consumption of 1.4 l water/day, the probability of new cancers occurrence is at least 2.4 additional cases for 25 years of exposure and maximum 4.61 cases for 35 years of exposure in the existing background of a 1 million people.

**Keywords**: trihalomethane, drinking water, water distribution system, exposure dose.

[1] Babes-Bolyai University, Faculty of Environmental Sciences and Engineering, Cluj-Napoca, Romania, e-mail: corneliahertia@yahoo.com

[2] Environmental Health Center Cluj-Napoca

## 1. INTRODUCTION

Interest regarding public health protection in terms of drinking water quality, requires raw water treatment according to the requirements specified in the national legislation. The European Directive 98/83/EC on water for human consumption is implemented in Romania by Law 458(rl)/2002 on drinking water quality and sets the maximum admitted limits for indicator and water quality parameters intended for human consumption. The final step of water purification is disinfection, a procedure for protecting drinking water against external contamination and re-growth of bacteria during distribution (Lee et al., 2004). The most common form of disinfection worldwide is represented by chlorination. This kind of disinfection process is the most commonly employed chemical disinfectant in drinking water nowadays (Lee et al., 2004).

Trihalomethanes (THMs) are organic compounds derived from methane by substitution of 3 hydrogen atoms with halogens. The most popular and studied forms of THMs are: chloroform ($CHCl_3$), dichlorbromoform ($CHCl_2Br$) dibromochloroform ($CHClBr_2$) and bromoform ($CHBr_3$). For Romania (EU), the maximum admitted limit according to the legislation in force is 100 µg/l for total THMs. Based on previous experimental models, Ristoiu et al. (2008) showed that higher concentrations of THMs are formed most likely in the water distribution network. Previous studies have revealed certain aspects related to the environment within the water distribution system, such as: occurrence of residual chlorine (generally from 3 mg/l and above), material of which pipes are made from (PVC), bio layer and microbial bioactivity at its level, may contribute to the occurrence of a complex system of reaction affecting THMs formation (Roman and Gurzau, 2012).

THMs from drinking water get inside the body through three major pathways: the digestive pathway through ingestion of tap water, the dermal pathway through dermal absorption during showering, bathing or swimming or the respiratory pathway through inhalation of vapors with trihalomethanes, so that the total exposure dose is represented by the aggregation of doses assimilated through the three pathways. Long term exposure to THMs both by ingestion, inhalation or dermal absorption shows that the individual exposure level depends on the contact pathway. Importance of the three different exposure routes is different because it deals with various concentrations and speciations of THMs present in water. Although water has distinct properties regarding human exposure and risk, in most countries THMs in drinking water are regulated based on the total concentration (Roman and Gurzau, 2012). Bassically, THMs exposure may result in non-carcinogenic and carcinogenic effects, thus prevention of human exposure to THMs being more then necessary (Gurzau et al., 2011). Recent research noted the risk and also the close relationship between exposure to THMs and adverse outcomes on the human body, especially the occurrence of vital organs cancers such as bladder and colorectal cancers (Backer et al., 2000, Wang et al., 2007). There are also toxicological and epidemiological studies that have focused on the effects of disinfection by products upon the reproductive function (low birth weight, premature birth, spontaneous miscarriage, stillbirth, congenital disorders of the central nervous and cardiovascular systems, oral cavity malformations) (Egorov et al., 2003, Nieuwenhuijsen et al., 2000).

The objective of this paper is to establish a relationship between the use of water from the public distribution system and exposure to THMs with possible risks upon human health. In this context, the study evaluated: the structure of the individual drinking water daily consumption at home and at work, the amount of water consumed in relation to different uses in the household, the THMs concentration levels and their species at different points in the water distribution network of Cluj Napoca and calculation of the exposure dose, the water intake and cancer risk calculated for a period of 25 and 35 years of exposure to chlorinated water.

## 2. MATERIAL AND METHODS

In 2009 a study was performed regarding the population exposure to THMs and as an important part of this study a questionnaire for assessment of water consumption was elaborated. The questionnaire included questions about the water consumption habits from the public distribution network for drinking and other purposes, at home or at work. The questionnaire was applied in 2009 for three different cities included in the study (Cluj Napoca, Targu Mures and Zalau) and 629 individuals were surveyed. For a population of 317.953 (according the 2002 census) in Cluj Napoca, statistical data showed that a margin of error of 5% at a confidence level of 85% and answers distribution of 50%, is needed for at least 208 subjects. It were chosen, randomly, 211 subjects, who were investigated, the only inclusion criterion was minimum 10 years of residency in the city. The subjects signed a written agreement to participate to the study, and it were respected the data privacy rules. Between September 2009 and January 2010, 21 water samples collected from different points in the distribution network of Cluj Napoca were analyzed, in order to mark out the concentration of THMs and their species. The water samples were collected in glass bottles of 20 ml, in which sodium thiosulphate ($Na_2S_2O_3$) was previously added and samples were stored at 4°C until analysis. The trihalomethanes analysis from water samples was carried out by GC-2010 gas chromatography with electron capture detector (GC-ECD) and a Shimadzu AOC 5000HS Autosampler. The exposure dose of THMs, daily intake of THMs and cancer risk were calculated using a calculation model developed by ATSDR (Agency for Toxic Substances and Disease Registry within the Center for Disease Control and Prevention, part of the U.S. Department of Health and Human Services), based on extrapolation mathematical models of high experimental doses in relation to low ambient doses. These calculations were performed for THMs concentrations identified in the water distribution network for the standard water intake from the distribution network of 2 l/day for adults and 1 l/day for children, and also for the average daily water intake in Cluj Napoca, resulted from the questionnaire (1.4 l/day for adults), for the same THMs concentrations. Databases and their processing were performed using Microsoft Excel version 5.0 software.

## 3. RESULTS AND DISCUSSION

The average age of the 211 subjects investigated based on a questionnaire was 43 years old, 40.8% were men and 59.2% women, of which over 80% had been lived in the city more than 20 years. Following the questionnaire application it was identified the fact that both bottled water and water from the distribution network are used for drinking, while for cooking or preparation of hot or cold beverages water from the distribution network is used in more than 90% (Fig. 1). According to the questionnaire, the average daily water intake for the subjects in study, adults is 1.4 l/day, 88% and 94.4% respectively of the respondents declare drinking coffee or tea as beverages prepared with tap water.

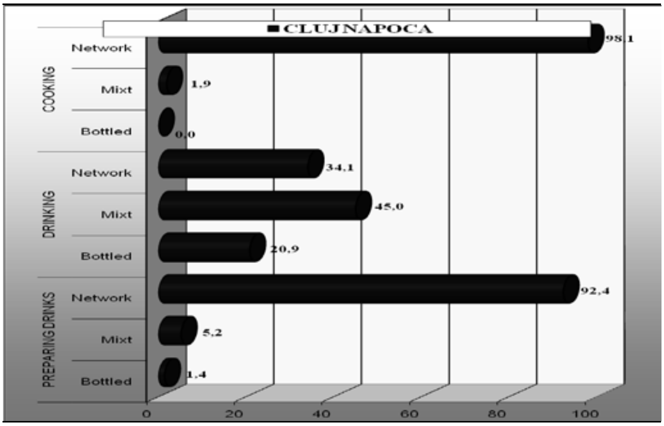


**Fig. 1.** ***Use of water sources***

The type of washing (bathing or shower), frequency, duration, and especially the temperature at which water is used are important factors in THMs cumulation in the human body. Fig. 2 shows that subjects investigated declare that they use showers (48.8%) between 4-7 times per week (61.1%) with duration of 0-15 minutes (64.9%) and at a temperature of 37-38°C defined in the questionnaire (88.2%).

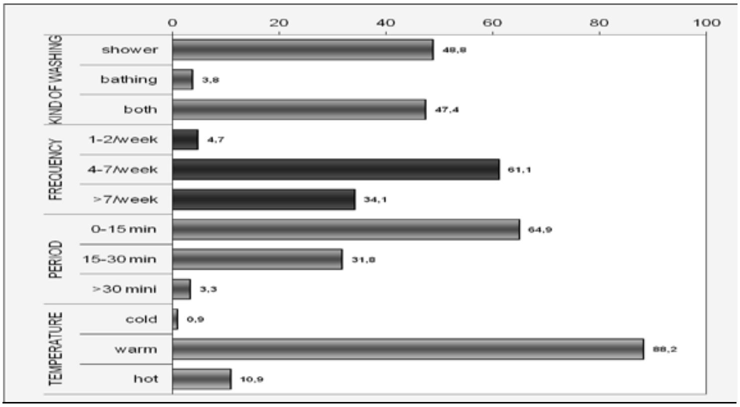


**Fig. 2.** ***Water consumption for personal hygiene***

In order to highlight the exposure dependent on THMs concentrations present in the water distribution network, water samples were analyzed. The monthly average concentrations of total THMs and their species have values between 64.16 (October) and 75.75 µg/l (November) (Fig. 3). Chloroform is the main identified component, which is responsible for increased levels of total THMs in the network. Compounds containing chlorine have identifiable values, but the bromoform compound was below the detection limit of the device in all analyzed samples (<4.00 µg/l). Previous studies have shown that THMs concentrations in the drinking water from the distribution system of Cluj-Napoca have a seasonal variation. Ristoiu et al., in 2008 showed that THMs concentrations have lower levels in winter than during summer (30 µg/l and 80 µg/l, respectively).

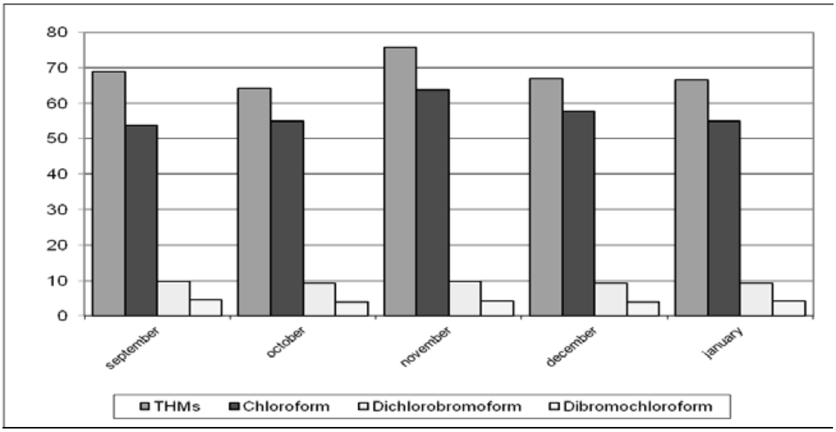


**Fig. 3.** ***Average monthly concentrations of total THMs and species in the water distribution network of Cluj Napoca, during September 2009-January 2010 (µg/l)***

Ingestion is an important route of human exposure to contaminants present in drinking water (Roman and Gurzau, 2012). An exposure dose is an estimate of the amount of a substance that one comes into contact after consumption of chemically-treated water and it is generally expressed in mg/kg body weight/day. Estimation of an exposure dose determines how much, how often and how long a person has contact with a certain amount of a chemical substance. Numerical estimates of risk use mathematical models applied to epidemiological or experimental data for carcinogenic effects (Roman and Gurzau, 2012), and these models assume that there are no threshold values for the chemical substances concentrations. Calculation for the intake, exposure and risk of cancer occurrence estimates a theoretical excess of cancer risk expressed as the proportion of a population that may be affected by the two types of substances capable to cause the development of cancer in terms of a lifetime exposure (but it can be also calculated for a determined period of exposure, in our case, 25 and 35 years by adding in the equation the exposure duration and report to the average life span) (Roman and Gurzau, 2012).

For the individuals investigated in Cluj-Napoca, the scenario was elaborated for the two major forms of THMs: chloroform and dibromochloroform, $CHCl_3$ known as probable human carcinogens, and $CHClBr_2$ as a possible human carcinogen (Batterman et al., 2002). For a standard water consumption of 2 l/day for adults and 1 l/day for children, at any of the concentrations analyzes and both for chloroform and dibromochloroform, the risk of cancer for adults, at 25-35 years of exposure is between 3.99E-06 and 6.59E-06 for chloroform; for dibromochloroform the cancer risk is between 3.43E-06 and 5.50E-06. For children, the risk of cancer is between 1.57E-05 and 2.59E-05 for chloroform and 4.80E-06 to 7.69E-06 for dibromochloroform (tables 1 and 2).

**Table 1.** ***Model for calculating the exposure dose for adults with a standard water consumption of 2 l/day***

| ***Model for calculating the exposure dose for an adult, aged between 19 and 65 years and a standard body weight of 70 kg – drinking water intake 2.0l/day*** | | | | | |
|---|---|---|---|---|---|
| ***Substance*** | ***Concentration*** | ***Calculated exposure dose (mg/kg/day)*** | ***Daily intake mg/day*** | ***Cancer risk at 25 years of exposure*** | ***Cancer risk at 35 years of exposure*** |
| chloroform | 68,80 | 1,97E-03 | 1,38E-01 | 4,29E-06 | 6,01E-06 |
| dibromochloroform | 4,58 | 1,31E-04 | 9,16E-03 | 3,93E-06 | **5,50E-06** |
| chloroform | 64,16 | 1,83E-03 | 1,28E-01 | **3,99E-06** | 5,58E-06 |
| dibromochloroform | 4,00 | 1,14E-04 | 8,00E-03 | **3,43E-06** | 4,80E-06 |
| chloroform | 75,75 | 2,16E-03 | 1,52E-01 | 4,71E-06 | **6,59E-06** |
| dibromochloroform | 4,11 | 1,17E-04 | 8,22E-03 | 3,52E-06 | 4,93E-06 |
| chloroform | 66,97 | 1,91E-03 | 1,34E-01 | 4,16E-06 | 5,83E-06 |
| dibromochloroform | 4,00 | 1,14E-04 | 8,00E-03 | **3,43E-06** | 4,80E-06 |
| chloroform | 66,63 | 1,90E-03 | 1,33E-01 | 4,14E-06 | 5,80E-06 |
| dibromochloroform | 4,13 | 1,18E-04 | 8,26E-03 | 3,54E-06 | 4,96E-06 |

**Table 2.** ***Model for calculating the exposure dose for children with a standard water consumption of 1 l/day***

| ***Model for calculating the exposure dose for a child, aged between 6 and 8 years years and a standard body weight of 25 kg – drinking water intake 1.0l/day*** | | | | | |
|---|---|---|---|---|---|
| ***Substance*** | ***Concentration*** | ***Calculated exposure dose (mg/kg/day)*** | ***Daily intake mg/day*** | ***Cancer risk at 25 years of exposure*** | ***Cancer risk at 35 years of exposure*** |
| chloroform | 68,80 | 2,75E-03 | 6,88E-02 | 1,68E-05 | 2,35E-05 |
| dibromochloroform | 4,58 | 1,83E-04 | 4,58E-03 | 5,50E-06 | **7,69E-06** |
| chloroform | 64,16 | 2,57E-03 | 6,42E-02 | **1,57E-05** | 2,19E-05 |
| dibromochloroform | 4,00 | 1,60E-04 | 4,00E-03 | 4,80E-06 | 6,72E-06 |
| chloroform | 75,75 | 3,03E-03 | 7,57E-02 | 1,85E-05 | **2,59E-05** |
| dibromochloroform | 4,11 | 1,64E-04 | 4,11E-03 | 4,93E-06 | 6,90E-06 |
| chloroform | 66,97 | 2,68E-03 | 6,70E-02 | 1,63E-05 | 2,29E-05 |
| dibromochloroform | 4,00 | 1,60E-04 | 4,00E-03 | **4,80E-06** | 6,72E-06 |
| chloroform | 66,63 | 2,67E-03 | 6,66E-02 | 1,63E-05 | 2,28E-05 |
| dibromochloroform | 4,13 | 1,65E-04 | 4,13E-03 | 4,96E-06 | 6,94E-06 |

In Table 3 are presented the results of exposure dose and cancer risk calculations for 25 - 35 years of exposure at the average daily intake of 1.4 l. In this situation, there is a very low prediction of cancer risk for adults, ranging from the lowest value 2.79E-06 to 4.61E-06 for 25-35 years of exposure to chloroform, and for 25-35 years of exposure dibromochloroform ranging between 2.40E-06 to 3.85E-06.

An estimated cancer risk of $1x10^{-6}$ predicts the probability of occurrence of a single additional cancer case in the existing background of a 1 million people.

**Table 3.** ***Model for calculating the exposure dose for adults with an average water consumption of 1.4 l/day***

| *Model for calculating the exposure dose for an adult, aged between 19 and 65 years and a standard body weight of 70 kg – drinking water intake 1.4 l/day* | | | | | |
|---|---|---|---|---|---|
| ***Substance*** | ***Concentration*** | ***Calculated exposure dose (mg/kg/day)*** | ***Daily intake mg/day*** | ***Cancer risk at 25 years of exposure*** | ***Cancer risk at 35 years of exposure*** |
| chloroform | 68,80 | 1,38E-03 | 9,63E-02 | 3,01E-06 | 4,21E-06 |
| dibromochloroform | 4,58 | 9,16E-05 | 6,41E-03 | 2,75E-06 | **3,85E-06** |
| chloroform | 64,16 | 1,28E-03 | 8,98E-02 | **2,79E-06** | 3,90E-06 |
| dibromochloroform | 4,00 | 8,00E-05 | 5,60E-03 | 2,40E-06 | 3,36E-06 |
| chloroform | 75,75 | 1,51E-03 | 1,06E-01 | 3,29E-06 | **4,61E-06** |
| dibromochloroform | 4,11 | 8,22E-05 | 5,75E-03 | 2,47E-06 | 3,45E-06 |
| chloroform | 66,97 | 1,34E-03 | 9,38E-02 | 2,92E-06 | 4,09E-06 |
| dibromochloroform | 4,00 | 8,00E-05 | 5,60E-03 | **2,40E-06** | 3,36E-06 |
| chloroform | 66,63 | 1,33E-03 | 9,33E-02 | 2,90E-06 | 4,06E-06 |
| dibromochloroform | 4,13 | 8,26E-05 | 5,78E-03 | 2,48E-06 | 3,47E-06 |

Doses associated with this estimated hypothetical risk may be by several orders of magnitude lower than the doses reported in the literature, causing carcinogenic effects. As a result, an estimated cancer risk lower than $10^{-6}$ may indicate that toxicological data will advocate that an excess risk of cancer most probably does not exist. Although we must admit the usefulness of these numerical risk estimates for the risk analysis, these estimates should be considered in the context of variables and assumptions involved in their derivation and in the broader context of biomedical opinions, genetic factors, and not least exposure conditions (Roman and Gurzau, 2012).

## 4. CONCLUSIONS

The questionnaire results show that people in Cluj-Napoca use for drinking both bottled water and water from the public distribution network, but for preparing food and beverages (coffee/tea) they use in proportion more than 90% water from the distribution network. The daily intake of hot drinks prepared with tap water is in average 200-400 ml. Water used for personal hygiene shows that besides the digestive pathway, inhalation and dermal contact lead to cumulative exposure to THMs. The concentration levels of THMs in the water in Cluj-Napoca city, during the investigated period (September 2009-January 2010) are below the maximum limit admitted by law (100 μg/l), the highest monthly average concentration was recorded in November (75.75 μg/l) and the lowest in October

(64.16 μg/l). Our study shows that the cancer risk to THMs is increasing related to the higher daily intake of the drinking water, being higher for chloroform compared to dibromochloroform. For the measured concentrations of chloroform and dibromochloroform in drinking water and the average daily consumption of 1.4 l water/day, the probability of new cancers occurrence is at least 2.4 additional cases for 25 years of exposure and 4.61 cases for 35 years of exposure in the existing background of a 1 million people.

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## REFERENCES

1. Backer L. C., Lan Q., Blount B. C., Nuckols J. R., Branch R., Lyu C. W., Kieszak S. M., Brinkman M. C., Gordon S. M., Flanders W. D., Romkes M., Cantor K. P., (2008), *Exogenous and endogenous determinants of blood trihalomethane levels after showering,* Environmental Health Perspective, *nr. 116*, 57-63,
2. Batterman S., Zhang L., Shugin W., Franzblau A., (2002), *Partition coefficients for the trihalomethanes among blood, urine, water, milk and air,* Science of the Total Environment, *nr. 284*, 237-247,
3. Egorov A.I., Tereschenko A.A., Altshul L.M., Vartiainen T., Samsonov D., LaBrecque B., Mäki-Paakkanen J., Drizhd N.L., Ford T.E., (2003), *Exposures to drinking water chlorination by-products in a Russian city,* International Journal of Hygiene Environment Health., *nr. 206(6),* 539-551,
4. Gurzău A.E., Popovici E., Pintea A., Dumitraşcu I., Pop C., Popa O., (2011), *Exposure Assessment to trihalomethanes from the epidemiological perspectives,* Carpathian Journal of Earth and Environmental Sciences, *vol. 6, nr. 1,* 5-12;
5. Lee S.C., Guo H., Lam S.M.J., Lau S.L.A., (2004), *Multipathway risk assessment on disinfection by-products of drinking water in Hong Kong,* Environmental Research, *nr. 94,* 47-56;
6. Nieuwenhuijsen M.J., Toledano M.B., Elliott P., (2000), *Uptake of chlorination disinfection by-products; a review and a discussion of its implications for exposure assessment in epidemiological studies,* Journal of Exposure Analytical Environment Epidemiology, *nr. 10, (6PT1),* 586-599,
7. Ristoiu D., Von Gunten U., Haydee Kovacs M., Chira R., (2008), *Factors affecting THM formation in the distribution system of Cluj, Romania,* GeoEcoMarina, *nr. 14,* 73-78,
8. Roman C.D. şi Gurzău A.E., (2012), *Evaluarea riscurilor expunerii la trihalometani din apa potabilă – studiu de caz,* Volum de lucrări a Conferinţei cu participare internaţională „Guvernanţă, Intelligence şi Securitate în secolul XXI", ISBN: 978-606-8330-11-2, 940-947,
9. Wang G. S., Deng Y. C., Lin T. F., (2007), *Cancer risk assessment from trihaloemthanes in drinking water,* Science of the Total Environment, *vol. 387,* 86-95,