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UNIVERSITATEA TEHNICA "GHEORGHE ASACHI" DIN IASI

„BABEŞ-BOLYAI" UNIVERSITY
CLUJ NAPOCA

Faculty of Environmental Science and Engineering

Assessment of trihalomethanes (THMs) exposure from drinking water and associated specific health risks

- abstract of PhD thesis -

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CLUJ NAPOCA - 2013

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The "DOCTORAL STUDIES FOR EUROPEAN PERFORMANCE IN RESEARCH AND INNOVATION (CUANTUMDOC)" POSDRU/107/1.5/S/79407 is a strategic project that has the following overall objective *"Application of management strategies, research and education to improve the initial training of future researchers through the doctoral studies program, according to the Bologna process, the development of specific research skills, but also general skills: research management, language and communication skills, documentation skills, writing, publishing and scientific communication, the use of modern means of ICT, entrepreneurship transfer of research results. Developing human capital for research and innovation will contribute to long-term doctoral training at European level with interdisciplinary concerns. The PhD financial support will ensure participation in doctoral programs in the country and research internships in research centers and universities in the EU. The mission of the project is the formation of a young researcher adapted to the market economy and new technologies, with theoretical, practical, economic and management knowledge at international level, which will promote sustainable development and protection of the environment."*

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Cluj Napoca,
August 2013

CONTENTS

The results of my experimental reasearch, general conclusions and selective references are presented in the abstract of the PhD thesis. The same notations for chapters, tables or figures as in the text of the PhD thesis were used for the abstract editing.

Keywords: **Trihalomethanes (THMs)**
Drinking water
Exposure assessment
Biomarker
Water consumption questionnaire
Exposure dose
Cancer risk

1. Introduction

Health effects in different susceptible (vulnerable) population groups related to environmental conditions are characterized in the risk assessment process. Risk assessment results are used to formulate, develop and implement strategies that lead primarily to lower exposure and associated risks.

As a stage in the risk assessment, exposure assessment of an individual to a chemical agent comprises a set of processes, i.e. qualitative or quantitative determination or estimation of the magnitude, frequency, duration and route of exposure to an agent and its derivatives of an organism, system or (sub) population.

Exposure assessment is followed, during the risk assessment process, by risk characterization, involving qualitative and quantitative determination of the probability of a known potential effect of an agent on an organism, system or (sub) population under certain exposure conditions. Full analysis of the exposure combines estimating the concentration in the environment (information on the source and mechanisms) with description of the population exposed according to the exposure profile. Biological measurements of the substances and their metabolites in tissues and fluids in the body can be used to estimate past or present exposure to chemicals where analytical methods are available.

Providing high quality drinking water involves management strategies to ensure the control of hazardous compounds from water. From the point of view of public health water contamination with various pollutants, must be analyzed in terms of their impact on health and therefore water intended for human consumption should not contain microorganisms or substances, which pose a risk to public health (98 / 83/EC, Law no. 458 (rl) / 2002).

The vast majority of water-related diseases are infectious. Microbiological surveillance of drinking water has been practiced since the early twentieth century in order to prevent water-borne diseases, the possibility of contamination with microorganisms in the water distribution system and deficiencies in treatment are known as the cause of outbreaks.

On the other hand, the role of water is important in reducing the incidence of waterborne infectious diseases. The influence of controlled water sources used for industrial and domestic needs and sanitation on the prevalence and severity of these diseases has been clearly demonstrated.

Currently debating quantity-quality for the water supply is about to be drawn in favor of quantity, most experts believing that water shortages lead to severe effects that can sometimes be on longer term. Degradation of water sources, especially their quantitative limitation and lack of accessibility determines that treating has to consider sources more or less contaminated by more complex means of technology. In most cases the presence of complex compounds as treatment byproducts consists in chemical mixtures, which are a real health risk, especially since the knowledge on their effects is still limited.

Microbiological safety of water for human consumption is also currently the main concern regarding water quality, but achieving this goal often involves risks generated by hazardous chemical compounds.

The most important step in water treatment for drinking and supply to the population, avoiding the risk of transmission of infectious diseases with epidemic character, is represented by disinfection.

To destroy pathogens is essential and very common to use chemical reagents such as chlorine. Disinfection with chlorine effectively reduces the number of pathogens, such as bacteria and viruses, this process using both surface and ground water. The use of chemical disinfectants in water treatment results in the formation of secondary compounds. The risk these secondary compounds pose on health is considered small compared to the risks associated with inadequate disinfection, and it is important that water treatment is not compromised in an attempt to control these byproducts (WHO, 2008, Lee et al., 2004).

It is known that any xenobiotic is a hazard and represents a risk; secondary compounds resulting from water disinfection by chlorination are no exception. Hazard begins with exposure and therefore growing evidence about health risks has been recorded.

Disinfection by-products (DBPs) are formed by two major classes of halogenated trihalomethanes (THMs) and haloacetic acids (HAAs), totaling over 600 compounds, usually found in water treated with chlorine. The most common and studied forms of THMs are chloroform (CHCl3), bromdichloromethame (CHCl2Br) dibromchlormethane (CHClBr2) and tribromomethane (CHBr3), ISO 10301/1997. They are both formed in the treatment plants and water supply systems, and are influenced by the type and dose of disinfectant, precursor charcteristics and concentration, temperature and pH of the water and the contact time. WHO and the European Community have included chloroform in the list of hazardous substances from water.

There are three major routes of human exposure to THMs: ingestion of chlorinated water by drinking, inhalation and dermal contact during personal hygiene, and various epidemiological and toxicological studies have shown that exposure to THMs may have adverse effects on human health. By far the most devastating effects are the carcinogenic ones (colon, bladder or rectum) with damage to various organs (stomach, brain, pancreas, lungs or liver) and reproductive (low birth weight, intrauterine developmental delay, pre-term birth, birth defects and stillbirth).

Our research presented in this thesis was substantiated by actions against contamination by carcinogens to ensure environmental quality and public health in accordance with the European strategic priorities on environment and safety and aims to find the exposure level of disinfection secondary compounds (trihalomethanes) in urban areas with different water sources and their treatment processes, in parallel we proposed risk characterization in exposure to these compounds by studying the effects on human health of populations with different degrees of exposure. To achieve these goals we had in mind the following:

• analysis of national and international data on exposure to THMs and health effects;
• developing the conceptual model of the mechanism of THMs formation during water treatment process;
• development of the experimental model for monitoring precursors (organic substances, chlorine) and carcinogenic compounds investigated - THMs in drinking water;
• assessment of the spatial distribution of THMs and exposure at receiver;
• development of the procedures for integrating information with populational character in the experimental model;
• estimation of the possible effects of exposure to THMs on population groups as priority hazardous substances from water in investigated areas by studying the characteristics of water consumption and the development of specific computational models.

The original results of the work were disseminated through presentation of 6 different papers (poster or oral presentations) at various International Conferences and Communication Sessions and by publishing one article ISI, 7 articles rated BDI, one article rated CNCSIS C and also by publishing a book alongside different experts in the field.

2.6. Qualitative aspects of drinking water supply of the population in Romania

In Romania, modernization, development and extension of the drinking water networks and sanitation is a measure required by the European Union; by 2025 the water supply systems need to reach high standards of performance, quality and quantity for the drinking water supplied to the population.

Synthesis of the water quality in Romania in 2011 showed that nationally, about 65% of the total population receives drinking water from the public water supply system, about 90% of urban and 33% of the rural population (www.rowater.ro).

The drinking water supply in centralized system of localities and population, in addition to the comfort it brings to the home, has the advantage of quality and safety, because of the possibilities of treatment, supervision and permanent control of the water entering the network. In terms of population served, national growth is directly proportional to the expansion of water distribution networks, registering a rate of coverage in 2009 of 55.2% of the total population (www.anrsc.ro).

Drinking water quality and the impact on human health have been the subject of numerous studies nationwide (Berkesy et al., 2008, Gurzau et al., 2013, Roman et al., 2013 Miclean et al., 2009). Overall, Romania faces problems regarding microbiological quality of water sources and the water supplied to the population. In this context, water disinfection, as well as treatment where appropriate also by other means, is mandatory and crucial to remove or mitigate infectious-type effects on public health.

In order to improve the quality of life and the protection of public health, it is necessary that the drinking water supply services are maintained at optimum operating standards, to provide consumers with safe, sanogenous water, which is sustainable by allocating priority investment funds from the local budgets.

3. Study design

Our research was conducted between 2009-2011 and addresses integrated issues of water quality and safety for consumers in the current context of EU policies that include THMs in drinking water on the list of priority hazardous substances.

Knowing the source, fate and concentration of THMs in drinking water in correlation with assessment of the effects on human health, is not only the basis for risk characterization, but also provides crucial information needed to make decisions on regulations, remediation, monitoring and management. In order to assess exposure to THMs in drinking water and effects upon human health in this study we proposed measurements, estimation models of parameters used and approximation of the current exposure conditions.

The main objectives associated with the project aims consist of creating specific databases concerning the variability of THMs concentrations as a result of the water treatment process, and their formation in the distribution network in urban areas, creating a mathematical model to characterize risk exposure to THMs in target human populations, exposure assessment at receiver level and biomonitoring of THMs.

Development of the experimental monitoring model of the studied precursors and compounds was performed in Cluj Napoca, Târgu-Mureş and Zalău. The criteria for which these localities were selected are the following:

- large urban areas with central water supply systems for over 30 years and where alternative water sources do not exist or are very limited;
- water treatment plants for drinking purpose with surface water sources (lakes and rivers);
- technologies with conventional treatment characteristics: pre-chlorination, coagulation/settling, filtration, disinfection with chlorine, individualized for each locality according to the type and quality of the water source (knowledge of the dynamics of organic contamination of water sources);
- condition of the distribution network.

This study consisted of several stages:

A first stage, obtained by measuring the concentrations of THMs and their precursors in water samples collected from each village at the treatment plant exit point and from key points of the distribution network.

The second phase consisted of detailed exposure assessment by collecting additional evidence, in specific fixed points of the distribution network of the three localities.

The third phase of the study consisted of interviews with consumer groups statistically representative for the population from the cities in study from numerical point of view, in terms of consumption habits and use of water from the distribution network.

The fourth step was to characterize risk exposure to THMs (carcinogenic effects) by using personalized mathematical model.

The last stage was the development of methods for identifying and evaluating exposure biomarkers in urine for a group of volunteers.

4. Working methods

For the present study, after a preliminary assessment of water quality in the three cities Cluj Napoca, Târgu-Mureş and Zalău, based on historical data, the water quality characterization aimed to determine the concentrations and variations of THMs and their species in certain sampling points during a given period. Due to the complex process of THMs formation, at the treatment station, as well as in the water distribution system, it was necessary to assess quantitatively the formation of THMs precursors in the raw water and treated water.

The determined sampling points were the following: source of raw water, pre-chlorinated water, filtered water (only in case of pre-chlorination), water leaving the water treatment plant and water in the distribution system. Sampling frequency was determined according to sampling points and parameters analyzed.

In 2009, in June, July and August water samples from the source were taken in 3-4 steps from Gilău, Vârşolț and Târgu-Mureş water treatment plants, and totaling 47 samples in the end. At the water treatment plants, samples were collected at the exit point of the treatment plant after chlorination for the analysis of THMs and their species (chloroform, bromodichloromethane, dibromchlormethane and tribromomethane). In addition, 51 samples were collected from the water in the tanks and the distribution systems of the three cities, so that coverage of the area to be uniform. The parameters analyzed were: oxidability, ammonia, nitrites, nitrates, free chlorine, total chlorine, trihalomethanes and their species (chloroform, bromodichloromethane, dibromchlormethane and tribromomethane).

In Cluj Napoca between September 15th, 2009- February 2nd, 2010 a total of 21 water samples were collected and analyzed from seven sampling points in the distribution network so as to cover all the important districts population clusters. Sampling was performed weekly using rotation points, each point being sampled 3 times. For these samples, we analyzed the following parameters: oxidability, ammonia, nitrites, nitrates, free chlorine, total chlorine, trihalomethanes and its species (chloroform, bromodichloromethane, dibromchlormethane and tribromomethane).

In Zalău and Târgu-Mureş in March-May 2011 samples were collected from the distribution network, weekly, from three points in the network, and these parameters were analyzed for: oxidability, ammonia, nitrites, nitrates, free chlorine, total chlorine, trihalomethanes and their species (chloroform, bromodichloromethane, dibromchlormethane and tribromomethane).

Water samples are considered momentary samples, they were collected manually and the sampling techniques were chosen according to ISO 5667/4-3.

Water samples for the determination of THMs precursors were collected according to ISO 5667/1-5, in clean plastic containers with screw cap with a capacity of 1 liter. The sample was taken by complete filling of the bottle, throwing the water, and refilling and closing of the container without leaving empty interior space, avoiding agitation.

4.3. Methods for analysis of the chemical parameters and indicators from raw and drinking water

For the analysis of the chemical parameters and indicators of collected water samples the following analysis standards were used: EN ISO 8467/2001 for the determination of the chemical oxygen (oxidability), SR ISO 7150-1/2001 for the determination of ammonia, SR EN 26777-91/2006 for the concentration of nitrites, SR ISO 7890-3/2000 for the concentration of nitrates, SR EN ISO 7393-2/2002 for determining the concentration of free residual and total chlorine and SR EN ISO 10301/2003 to determine the concentrations of total THMs and their species (chloroform, bromodichloromethane, dibromochloromethane and tribromomethane).

4.4. Methodology based on questionnaire investigation on water consumption and related habits in the population

Realistic estimates in terms of exposure to contaminants in drinking water require accurate information with respect to quantity and frequency of drinking water consumption throughout the day. A questionnaire was designed, which included questions about the habits of consuming water for drinking and other uses of the water at home and at work. The study was conducted during 2009. 629 subjects were investigated by questionnaire from the three cities covered by the study: Cluj Napoca (211 subjects), Târgu-Mureş (209 subjects) and Zalău (209 subjects). The number of representative subjects for each locality in order to have a margin of error of 5%, a confidence level of 85% and a 50% response distribution is at least 208 subjects for each locality. Therefore the subjects were randomly chosen, the only criterion for inclusion was at least 10 years of residence in the city. Selected subjects were informed on the purpose of the study and signed a written agreement to participate in the study, respecting privacy rules.

4.5. Dose calculation for THMs exposure in drinking water and the risk of cancer

Calculation of the exposure dose and the daily intake was done using the latest model for calculation of the doses prepared by ATSDR (Agency for Toxic Substances and Disease Recording, of the Center for Disease Control belonging to the Department of Health and Human Services of the U.S.).

In our study, the dose of exposure and daily intake for chloroform was calculated for ingestion and inhalation in adults with standard weight of 70 kg using the formula given by ATSDR.

Where dermal exposure is considered, the standard calculation program does not generate results, and we used a computational model adapted from Wang et al., (2007).

Calculation of cancer risk from <u>ingestion</u> started from the calculation of the daily exposure dose, and use of the standard rate of ingestion of 2 liters water/day and a standard body weight of 70 kg in adults.

Calculation of cancer risk from <u>inhalation</u> was made by usimg the ATSDR model. To calculate the concentrations of chloroform (vapor) in the air we used the formula given by Sanders (2002).

Calculation of cancer risk through <u>dermal exposure</u> was based on the daily exposure dose calculation for an adult of 70 kg and an exposure time of 10 minutes using the formula given by Wang (Wang et al., 2007). Cancer risk was calculated using the formula from the ATSDR program.

This calculation estimates a theoretical excess of cancer risk expressed as the proportion of the population that may be affected by the substance and capable of causing the development of cancer, in case of lifetime exposure (but it can be calculated for a certain exposure period, in our case, 25 and 35 years by entering in the equation for calculating the duration of exposure and with reference to the average lifespan).

These estimates should be viewed in the context of variables and assumptions involved in their derivation and in the broader context of biomedical opinion, genetic factors, and not least, the conditions of exposure.

4.6. The study of THMs concentrations in human urine

For this study we chose two different populational groups, each consisting of 9 persons. The first group of people without exposure to THMs, was selected from the town of Mocod, Nasaud County and the second population group is the one with exposure to THMs from Floreşti and Cluj Napoca, Cluj County. Each group consisted of both men and women, because urine samples can be influenced by the sex of the subjects. The population group without exposure to THMs in drinking water is supplied exclusively from individual sources where water is not subject to water treatment processes, including chlorination. The second group included in this study was selected from urban environment and exposed to THMs from water, as all 9 subjects used water from the water treatment plant Gilău, in Cluj County.

The subjects selected were healthy volunteers with no reported medical history, who expressed their written consent to participate in this study. The study design consisted of:

•collection of a sample of cold water and one of hot water at home;

•filling up a questionnaire on water use;

•applying a questionnaire to obtain information about the last exposure to THMs linked to the collection of urine samples.

Unexposed subjects were visited once at home, in Mocod, in order to collect the written consent, water and urine samples, while applying questionnaires.

The group of subjects exposed to THMs was investigated in two different experimental conditions, during two consecutive days: the first step consisted in using network water in limited quantity and the second step in using network water in higher quantity for drinking, cooking and personal hygiene.

The urine sample for THMs analysis was collected as the first urine of the morning, after 24 hours of exposure / non-Exposure to drinking water.

Analysis of the total THMs levels and compounds in urine was performed 1-3 hours after samples collection, which were kept cool (4^0 C) until analysis. For analysis, we added 3 g of potassium chloride to vials and transferred 12 ml of urine, after it was stored at room temperature. The sample was placed in the automatic sampler and heated to 85^0C for 40 minutes, then injected in the gas phase. For each set of six samples analyzed, a blank with distilled water was performed and a control sample by adding 2 ml of THM solution with a concentration of 200 mg / ml was also performed. Analysis of water and urine samples to determine THMs and compounds was performed by GC-2010 gas chromatography with electron capture (GC-ECD) and an automatic sampler Shimadzu AOC 5000HS.

We calculated intake of THMs through ingestion and inhalation for measured THMs values from the water samples taken from the water tap in subjects' homes. The concentrations of THMs considered were chloroform and bromodichloromethane, which were measured in cold water for ingestion and measured in hot water for inhalation. We also used individual data from the applied questionnaire regarding water consumption, duration of shower / bath and bathroom size.

5. Results

5.1. Drinking water quality in Cluj Napoca, Zalău and Târgu-Mureş, in terms of concentrations of THMs and precursors

Assessment of exposure to trihalomethanes (THMs) and calculation of the exposure dose, the daily intake and the risk of cancer was made for the population of the three municipalities in the study. Because THMs generation is dependent on treatment steps efficiency prior to water chlorination, for each centralized water supply the evolution of THMs precursors (nitrogen organic compounds and free residual chlorine) were investigated, in both the treatment plant and the network distribution. The purpose of these measurements was to analyze the efficiency of the treatment plants and estimate the levels of precursors which lead to the formation of THMs, both at the exit point of the water treatment plant and along the water supply network.

Results showed common and also specific aspects for the three central water distribution systems. Choice of the processes for drinking water treatment is determined by the raw water quality (mainly microbiological quality), and also to the length and condition of distribution networks.

The localities studied (Cluj Napoca, Zalău and Târgu-Mureş) have raw water sources consisting of surface water bodies with varying degrees of contamination. Their treatment is performed in the Gilău water treatment plant, Cluj County; Vârşolț treatment plant for Salaj County and Târgu-Mureş treatment plant for Mures County.

The investigated water sources show more or less variable chemical characteristics, the treatment consisting of conventional processes: coagulation/settling, rapid filtration and disinfection with chlorine. In the case of Vârşolț treatment plant a pretreatment step (pre-chlorination) is added before coagulation / settling, and for the water treatment plant in Târgu-Mureş the use of potassium permanganate oxidation since 2010, before the pre-treatment consisting of chlorination.

The water distribution systems in the three cities, operating for over 30 years at the time of the study, were in the process of modernization and replacing of the old pipelines.

Quantitative and qualitative evaluation of THMs and precursors in the central water supply systems of Cluj Napoca, Târgu-Mureş and Zalău was done by collecting a total of 137 water samples and analyzing them for the following parameters: oxidability, ammonia, nitrite, nitrates, free and total chlorine, THMs (chloroform, bromodichloromethane, dibromchloromethane and tribromomethane). The selection of the sampling points was done in order to cover all the treatment steps in the water treatment plant and distribution system.

Selected parameters were analyzed in raw water, treated water and the network water to provide information not only on the contamination of drinking water, but also on the possibilities of generating THMs based on the nitrogen cycle.

In a first step, June to August 2009, water samples were collected in 3-4 stages, from the treatment steps and from the distribution network in Cluj Napoca, Zalău and Târgu-Mureş - total 98 samples.

In the second stage, water samples were taken only from the distribution network, as follows:

- Cluj Napoca, September 2009-February 2010 - 21 samples,
- Zalău and Târgu-Mureş, March-May 2011, by 9 samples from each city.

Water samples were taken from the distribution network of Târgu-Mureş and Zalău to measure concentrations of THMs and their precursors in those points in the network where the analysis phase in the summer of 2009 identified elevated levels in the network.

Calculation of the efficiency of a treatment plants was performed for THMs precursors (oxidability, ammonia, nitrite and nitrate) and assumes a percentage estimation of the level of an observed parameter that remained in the treated water following a technological process.

5.1.1. The central water supply in Cluj Napoca

At the Gilău water treatment plant, at the time of the study, the raw water came from Tarnița lake. In order to assess exposure to THMs from drinking water for the city of Cluj Napoca, precursors were analyzed in the technology flow and distribution network of the city, totaling 40 water samples. At each sampling period (June to August), a sample was taken from the raw water entering the water treatment plant, a sample from the settled water, one of filtered water and one from the water leaving the treatment plant (full treated, chlorinated). At city level, seven tanks and 11 points in the network were sampled, which covers all major districts in size, and also in number of inhabitants.

The results showed that water sources investigated showed moderate variable characteristics regarding nitrogenous organic matter as a precursor of THMs. Analysis of the water treatment technology flow has shown that there is a possibility of generating THMs, but it is lower in the treatment plants.

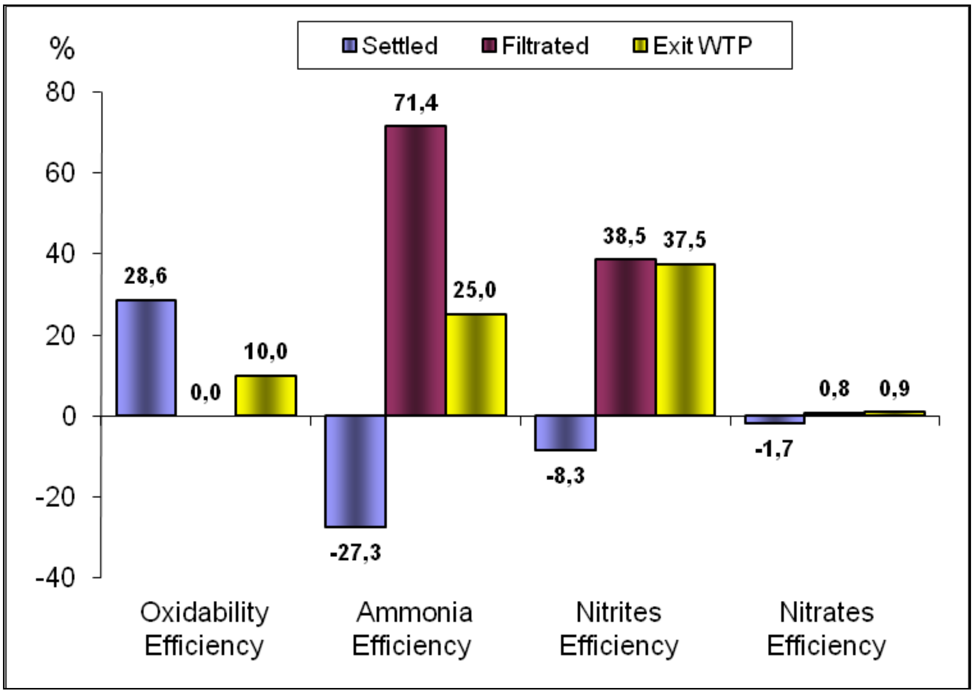
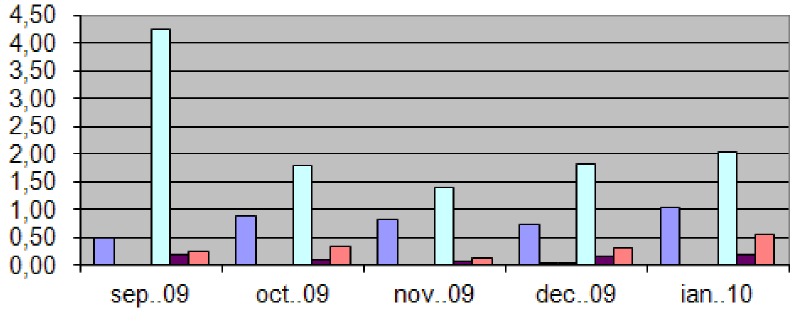


Figure 12. The efficiency of reduction of organic nitrogen compounds at Gilău water treatment plant – 17.07.2009

For the treatment steps to be effective, they need to reduce the levels of indicator parameters (oxidability, nitrites) as treatment processes go on. In the case of the Gilău water treatment plant, the efficiencies (%) for reduction of the nitrogenous organic matter in various stages of treatment, were calculated for oxidability, ammonia, nitrites, and nitrates and ranged from 0-70% (Fig. 12).

In fig. 13 we present the monthly average concentrations for all sampling points and analyzed parameters, considered precursors of THMs. The figure shows that oxidability and nitrates had the highest average value in January 2010 (1.46 mg / l, respectively 1.02 mg / l). For ammonia and nitrite the average value was not calculated, as the majority of the measurements showed values that were below the detection limit of the analytical method (<0.003 mg / l and <0.005 mg / l).



	01.09.2009	01.10.2009	01.11.2009	01.12.2009	01.01.2010
Oxidability mg O2/l	0,48	0,87	0,81	0,72	1,02
Ammonia mg NH4/l				0,01	
Nitrites mg NO2/l				0,01	
Nitrates mg NO3/l	4,26	1,79	1,39	1,82	2,02
Free chlorine mg Cl2/l	0,17	0,10	0,06	0,14	0,19
Total chlorine mg Cl2/l	0,23	0,33	0,11	0,31	0,54

Figure 13. Levels of THMs precursors in drinking water from distribution network of Cluj Napoca, September 2009-February 2010 (monthly averages)

Regarding free residual chlorine, it had low monthly averages between 0,06 and 0,19 mg/l. Free chlorine/total chlorine ratio was below 80% (between 30% and 45%).

5.1.2. The central water supply in Zalău

At each sampling stage (June-August 2009) a sample of raw water from the water treatment plant entry point, a sample of settled water, one from the filtered water and one from water leaving the treatment plant (chlorinated) were taken. At city level, 3 large tanks and 8 different points in the network were sampled, which covers all major districts in size and in number of inhabitants.

In the treatment plant filtering was efficient, with a positive output only in correction of the oxidability and nitrite level, as for reducing the level of ammonia in the water it had a negative output, having no effect on nitrates levels. Water oxidability was reduced by 42.53% through decantation and by 20.2% through chlorination, the disinfection process had a negative output on nitrate levels, even generating an increase of their content in the water exiting the water treatment plant (fig. 17).

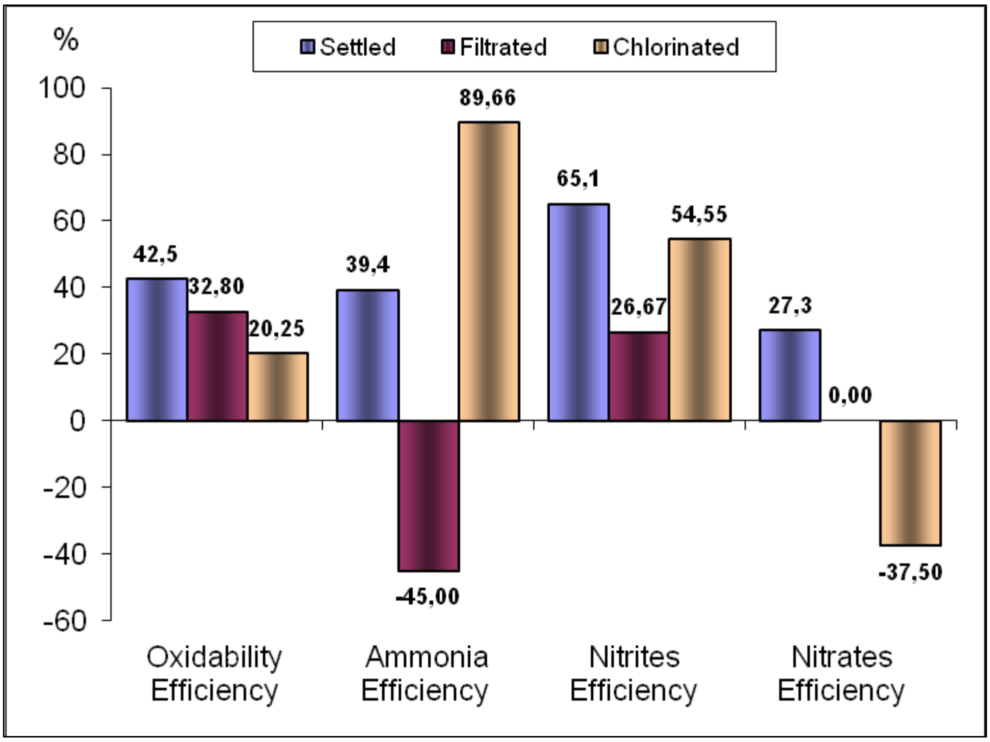


Figure 17. The efficiency of reduction of organic nitrogen compounds at Vârşolț water treatment plant – 15.07.2009

Regarding the monthly values of THMs in the water supply system, the highest concentrations were the following:

• June: treatment plant exit - 50,63 mg / l tank (Brădet) -75.64 mg / l network (Mihai Viteazul str.) -103.58 mg / l,

• July: treatment plant exit - 59,96 mg / l tank (Dumbrava) -78.67 mg / l Network (Mihai Viteazul str.) -86.02 mg / l,

• August: treatment plant exit - 68 treatment, 25 mg / l tank (Ortelec) – 91,34 mg / l, and in 5 points in the network has surpassed the maximum allowable limit, with values up to 116,79 mg / l (Table 13).

Table 13. Sampling points and results of THMs and species – Zalău June-August 2009

	THMs	Chloroform	Bromdichlormethane	Dibromchlormethane	Tribromometane
25.06.2009	µg/l	µg/l	µg/l	µg/l	µg/l
Exit water treatment plant	50,63	28,15	15,67	6,81	< 4,00
Reservoir Brădet	75,64	46,11	21,34	8,19	< 4,00
Network str. A. Iancu	78,19	47,50	21,91	8,78	< 4,00
Network P-ța 1 Dec. 1918	88,64	57,32	22,54	8,78	< 4,00

Network str. Mihai Viteazul	103,58	67,05	26,9	9,63	< 4,00
Network str. Lt. Col. Pretorian	71,72	42,74	20,79	8,19	< 4,00
15.07.2009					
Exit WTP	59,96	37,68	15,90	6,38	< 4,00
Reservoir Brădet	75,76	45,76	21,65	8,35	< 4,00
Network str. A. Iancu	78,89	47,70	22,50	8,69	< 4,00
Network P-ța 1 Dec. 1918	80,11	48,80	22,60	8,71	< 4,00
Network str. Mihai Viteazul	86,02	52,01	24,44	9,57	< 4,00
Reservoir Dumbrava	78,67	47,85	22,19	8,63	< 4,00
05.08.2009					
Exit WTP	68,25	41,24	17,97	7,55	1,47
Reservoir Ortelec	91,34	56,14	24,21	9,61	1,37
Network str. Dumbrava	9,04	9,04	<4,00	<4,00	<1,00
Network str. Mihai Viteazul	112,57	73,14	28,10	10,03	1,30
Network str. T. Vladimirescu	116,79	76,41	28,80	10,32	1,26
Network str. Mihai Viteazul nr. 23A	102,01	64,87	26,12	9,68	1,32
Network str. Torentului	100,37	63,03	25,95	9,92	1,46
Network str. A. Iancu	102,24	63,02	26,97	10,70	1,55

5.1.3. The central water supply in Târgu-Mureş

Târgu-Mureş water treatment plant processes water from Mureş river, a raw water that is characterized by a significant microbiological contamination and greater instability of the indicator parameters (Domahidi, 1996). Chlorination is done only after the pre-oxidation, coagulation, settling and filtration of the water, as re-chlorination is not performed for the tanks in the city.

At each sampling period (June to August), a sample of the raw water from the water entering the water treatment plant, a sample from the settled water, one from the filtered water, one from the chlorinated water and one from the output of the treatment plant were taken. At city level, 4 tanks and 11 different points in the network were sampled, which covers all major districts in size, and in number of inhabitants.

Târgu-Mureş treatment plant processes water from a river, therefore this process must be dynamic, adapted to the qualitative changes of the water source that occur very quickly. Efficiency of the technological steps varied depending on the specific stage and the parameter studied. Thus, the settling process has shown a positive efficiency of 3.6% for the correction of the level of nitrates up to 63.5% with regard to reducing the amount of nitrite, whilst filtration was most effective in reducing the level of ammonia, with a negative output for nitrite and nitrate. Chlorination positively influenced oxidability, but especially the reduction of ammonia and nitrite. In order to reduce the latter, a very large efficiency of 92.1% was calculated, which instead favored an increase in the amount of nitrate in the water (Fig. 19).

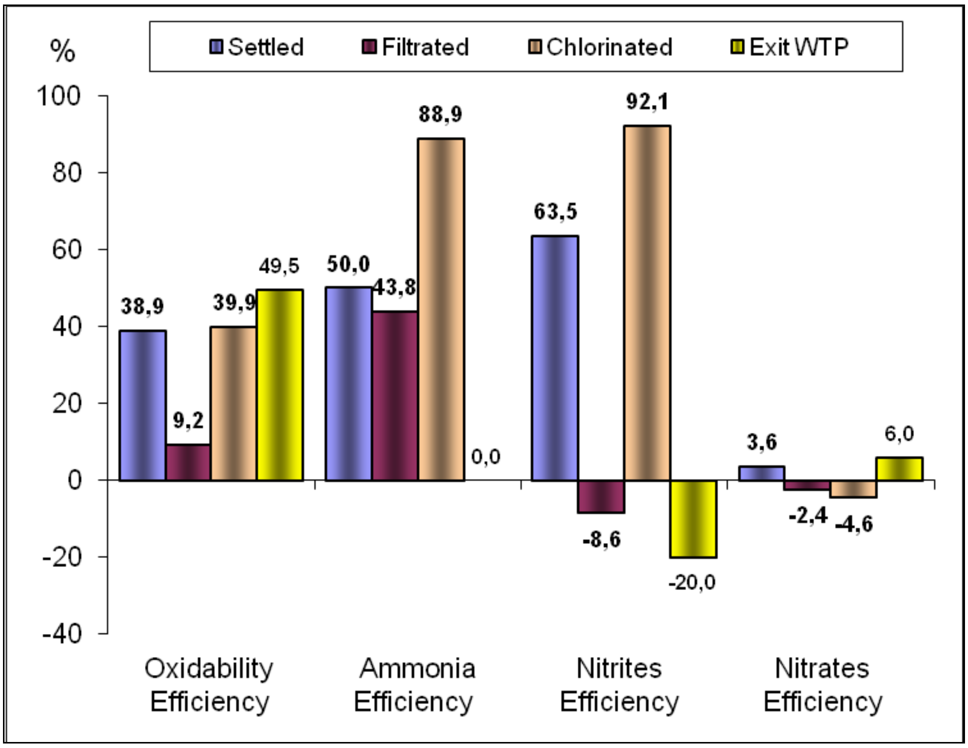


Figure 17. The efficiency of reduction of organic nitrogen compounds at Vârşolț water treatment plant – 15.07.2009

Regarding the monthly values of THMs in the water supply system, the highest observed concentrations were the following:

• June: the concentration of THMs leaving the treatment plant - 61.60 mg / l, reservoir (Castle) - 72.11 mg / l, and network - 89.24 mg / l (Papiu Ilarian str.)

• July: treatment plant exit point - 82.87 mg / l tank (Trebely) - 92.24 mg / l, and network - 90.64 mg / l (Bărăganului str.)

• August: treatment plant exit point - 80.18 mg / l, and the network were recorded 2 values above the limit of 100 mg / l, Gheorghe Doja Street, no.287 and no. 89, with concentrations of 101.58 mg / l and 100.95 mg / l (Table 20).

Table 20. Sampling points and results of THMs and species – Târgu-Mureş, June-August 2009

	THMs	Chloroform	Bromdichlormethane	Dibromchlormethane	Tribromomethane
16.06.2009	µg/l	µg/l	µg/l	µg/l	µg/l
Exit WTP	61,60	50,17	11,43	< 4,00	< 4,00
Reservoir Castel	72,11	60,16	11,95	< 4,00	< 4,00
Reservoir Verii	69,33	57,13	12,20	< 4,00	< 4,00
Network - str. Gh.Doja	71,42	54,69	12,05	4,68	< 4,00
Network str. Papiu Ilarian	89,24	71,13	13,36	4,75	< 4,00
Network str. Apicultorilor	76,03	63,05	12,98	< 4,00	< 4,00
13.07.2009					
Exit WTP	82,87	67,19	11,32	4,36	< 4,00
Reservoir Suceava	88,01	70,26	13,07	4,68	< 4,00
Reservoir Trebely	92,24	74,44	13,30	4,50	< 4,00
Network str. Bărăganului	90,64	74,03	12,24	4,37	< 4,00
Network str. Godeanu	81,4	65,08	11,99	4,39	< 4,00
Network str. Gh. Marinescu	82,33	65,77	13,83	4,73	< 4,00
12.08.2009					
Exit WTP	80,18	60,16	15,12	4,90	<1,00
Network str. Voiniceşti	79,23	59,55	14,82	4,86	<1,00
Network str. Barajului	92,63	71,26	16,33	5,04	<1,00
Network str. Gh. Doja (nr. 287)	101,58	78,24	18,09	5,25	<1,00
Network str. Gh. Doja (nr. 89)	100,95	77,40	18,40	5,15	<1,00
Network str. 22 Dec. 1989	85,88	64,78	15,95	5,15	<1,00

Evaluation of THMs precursors (organic matter and chlorine) demonstrated that the generation of THMs continues in the distribution network, increasing where re-chlorination is used for the water storage tanks in the city (Zalău), and where they were associated with exceedings of the maximum allowable concentration (6 samples from points within the distribution network in Zalău, with values ranging from 100.37 mg / l and 116.79 mg / l; in Târgu-Mureş two samples network showed values of 100.95 and 101.58 respectively mg / l). For Cluj Napoca, the levels of THMs do not exceed the maximum allowable limit of 100 mg / l in any of the analyzed samples (treatment plant exit point, reservoirs and distribution network). THMs generation can be prevented at the end of the treatment process or in the network by previous rigorous treatment that reduces the content of organic matter, or by the existence of a distribution network in a good state of maintenance. We identified as a possible cause of generating THMs in the distribution system, the existence of biofilms containing nitrogenous organic matter, which increases chlorine demand for reaching the microbiological safety threshold and also increase the risk of THMs formation in the network.

As a comparison between the three localities, we mention that elevated concentrations of THMs in Zalău, followed by Târgu-Mureş and Cluj Napoca were identified. In the three localities, THMs formation begins in the treatment plant together with chlorination and continues until a point in the distribution network, these values increase until the tank level and then tend to decrease in the network. Regarding the presence of these THMs species, they were not identified consistently in all places and in all water samples. The predominant species identified in the highest concentrations in all water samples was chloroform, the rarest species identified at the lowest concentrations was tribromomethane. High levels of total THMs are strongly influenced by the quality of raw water, treatment plant performance, process of re-chlorination or hyper-chlorination of the storage tanks and the condition of the drinking water distribution pipes. The treatment plants studied and the technologies performed, provide at the exit point of the treatment plant water, which meets the quality standards from the point of view of the analized indicators, although the use of additional treatment processes created the premises for the formation of THMs with secondary effects upon population health. In order to assess exposure to THMs in the water and risk characterization, it is necessary to accurately determine the predominant exposure routes.

5.3. The results of questionnaire-based study conducted in three cities under study

In order to protect public health, the ideal situation is represented by a frequent monitoring of the essential criteria of water quality: levels of inactivation for microorganisms, turbidity and THMs levels in chlorinated water concomitant with minimal levels of free residual chlorine and control of bacterial contamination in the distribution system.

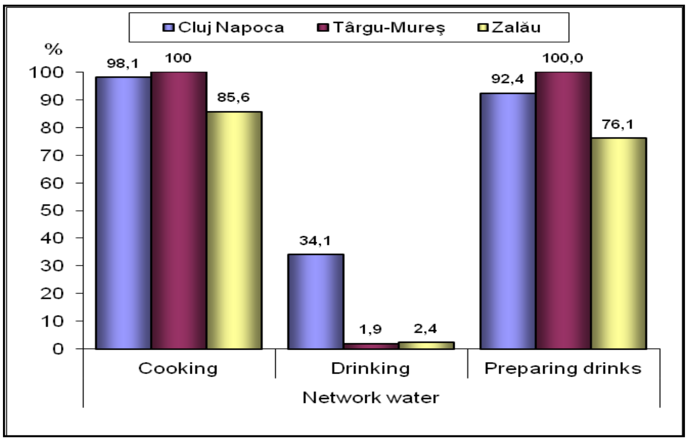
The questionnaire-based study conducted in July-September 2009 investigated 629 subjects from three localities under study: Cluj Napoca (211 subjects), Târgu-Mureş (209 subjects) and Zalău (209 subjects), randomly chosen, the only inclusion criterion was residency for at least 10 years. They were questioned about the use of water for drinking and other purposes at home and at work, maintaining privacy, and participants signed a participation agreement.

The first section of the questionnaire for individual water consumption (Section A) included questions about demographic characteristics, sex of the participant, age and years of education (years of school).

Sections B and C of the applied questionnaire provided information about their consumption of water both at home and at work. These sections were related to the type of water consumed (central distribution, from spring or bottled), water used for cooking, drinking and preparing beverages, the average consumption and opinion about the aesthetic characteristics of water (taste, smell).

Section D of the questionnaire applied to the 629 people includes questions about their lifestyle and other exposures to water, through the type of personal hygiene (shower, bath, or both), duration, temperature of water during hygiene procedures, the frequency a person goes to interior or exterior water pools and the organoleptic characteristics of the water from these pools.

The results showed that over 80% of the interviewed subjects stated that they reside in the city for over 20 years. The group of subjects surveyed had an average age of 42 years, consisting mostly of women (64%), most subjects with higher education. The type of water used at home or at work shows large differences between the subjects investigated. Significant associations were observed between water consumption by age, gender and places of residence of the subjects. Overall, for the three cities, tap water is used for preparing food, beverages (coffee, tea), the water used for drinking being mainly bottled water (fig. 24).



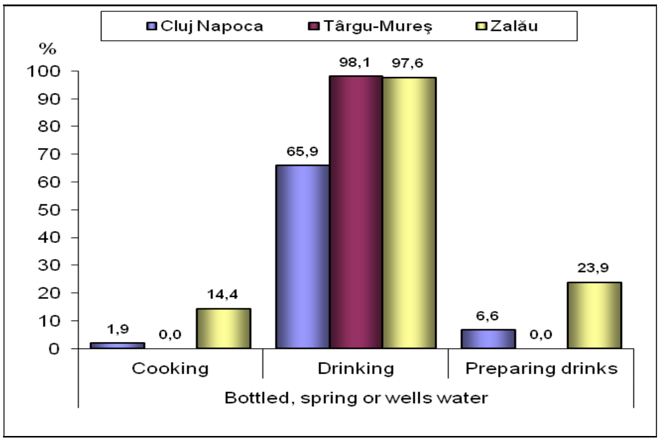
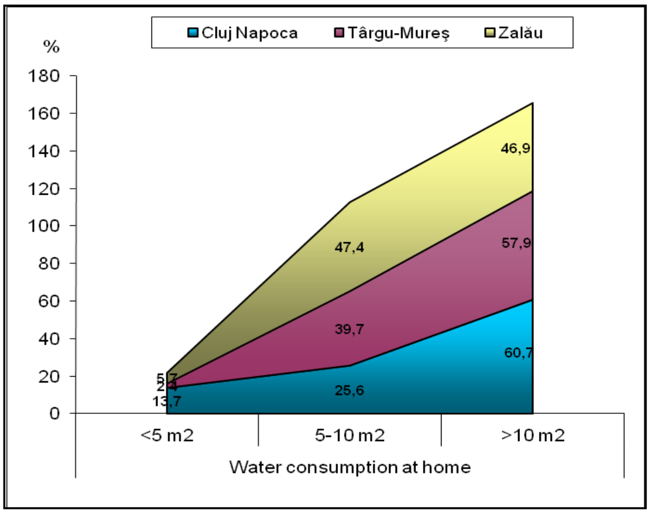


Figure 24. General information about water use in homes

In most cases the subject's estimation of water quality is strongly influenced by its organoleptic properties, in particular taste, that encourage or limit consumption.

Average household water consumption exceeds 10 m^3 in all three localities, and bottled water consumption for Cluj Napoca is less than 7 l / week for 42.2% of the population in study and for the localities Târgu-Mureş and Zalău greater than 6 l / week for 92.3% and 87.1% of respondents (fig. 25).



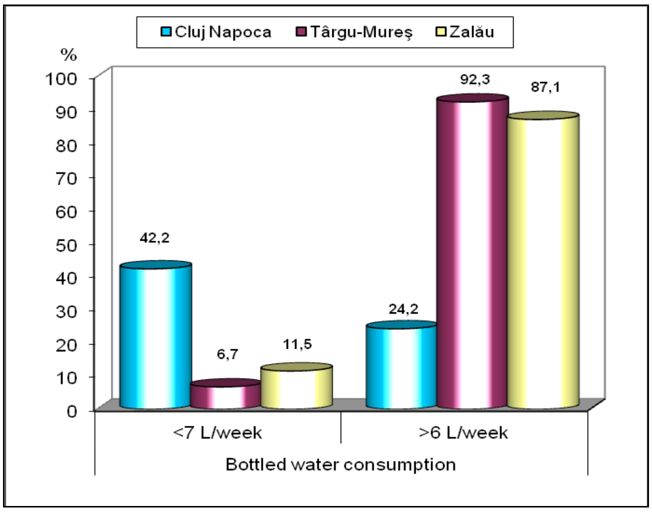


Figure 25. The average consumption of water/day

Differentiation between subjects by gender shows that daily water consumption in males is higher compared to the females in the three cities in study, the difference being greater for Târgu-Mureş and Zalău (fig. 26).

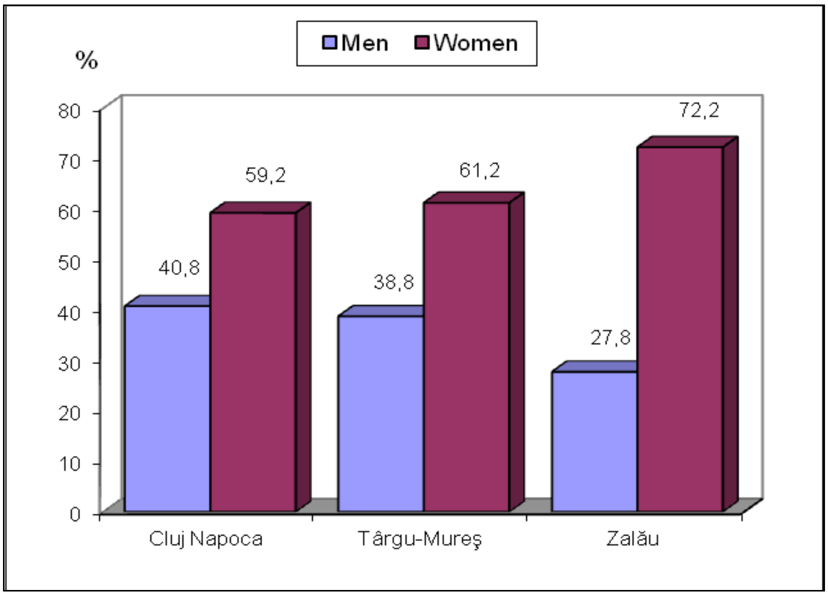


Figure 26. Average consumption of water on localities and sexes

In Cluj Napoca over 80% of those questioned said that tap water has no taste or odor of chlorine, while in Târgu-Mureş and Zalău over 30% of respondents refuse to drink water from the public network because of the smell or taste of chlorine.

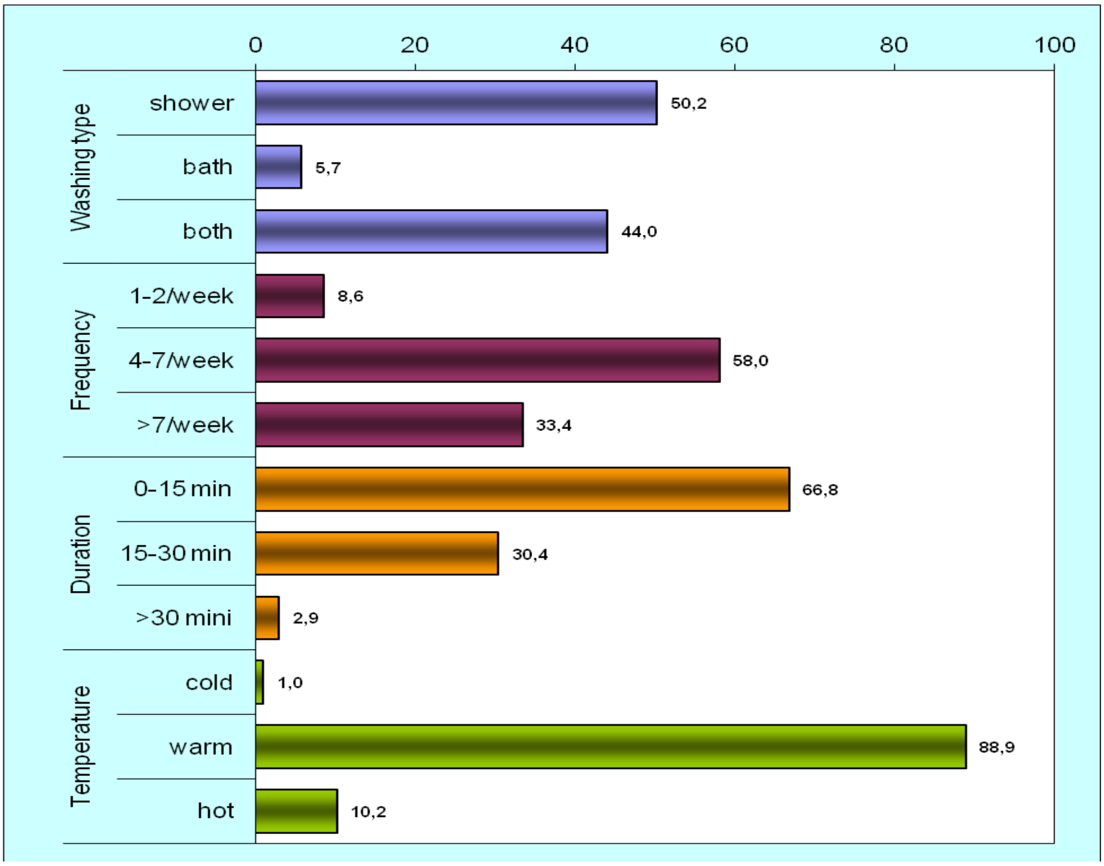


Figure 28. Water use for personal hygiene at total questioned persons (Gurzău and colab., 2011)

Whatever the organoleptic characteristics of the network water, people use it for personal hygiene, most of those in the study saying that they take a shower / bath (50.2% / 44.0%) with a frequency of 4-7 times per week (58 %), and a maximum duration of 15 minutes (66.8%) at a water temperature of about 37-38^{0}C (88.9%).

The general trend is to decrease the consumption of drinking water from the public network supply, therefore, the route of exposure to THMs in water is through personal hygiene.

At present, it is considered that ensuring a sufficient water quantity is more important than quality especially taste, considering that the lack of water and sanitation lead to diseases that can be devastating to human communities, stopping the water supply of a community is a risky decision in terms of public health.

The taste and smell of tap water (organoleptic characteristics) were correlated with elevated concentrations of THMs, and two thirds of those surveyed had measured concentrations of THMs in water above 70 mg / l, which is signaled by disturbing smell or taste of the water (table 25). Beyond the formation of secondary disinfection compounds (THMs), the chlorine taste and odor problem is what most consumers are dissatisfied with when drinking water (Milmo, 2006). Because of the chlorine taste of the water from the network, consumers prefer bottled water, but this leads to higher economic and environmental costs (Milmo, 2006).

Researchers who studied the indirect sensorial effects of water chlorination established a relationship between taste / odor of water and generation of disinfection byproducts (Heim and Dietrich, 2007).

Table 25. THMs concentrations and organoleptic characteristics of drinking water (Gurzău and colab., 2011)

Trihalomethanes	N	Unpleasant smell (%)	Unpleasant taste (%)
<70µg/L	209	13.88	10.05
>70µg/L	418	41.87	40.19

The risk to human health from exposure to THMs is associated with the variability of the ingestion of water, life expectancy, cold water temperature, water temperature in the shower, the amount of free residual chlorine, THMs formation kinetics, quantity and characteristics of organic substances in water, size of bathroom or shower, water flow, dermal absorption of THMs or shower duration (Xu and Weisel, 2006 Chowdhury and Champagne, 2009).

5.4. Risk characterization for THMs exposure – cancer risk calculation

Risk characterization, the final step of risk assessment involves characterizing the potential health effects that occur in contact with a particular contaminant. Using the model mentioned above (ATSDR), we calculated the cancer risk for 25 to 35 years of exposure to chloroform in drinking water through the digestive, inhalant and dermal routes. The model used the average concentrations of chloroform in the water distribution network for each city as follows:

- Cluj Napoca - September 2009-February 2010 (21 samples),
- Zalău - June-August 2009 and March-May 2011 (22 samples),
- Târgu-Mureş - June-August 2009 and March-May 2011 (20 samples).

These periods were considered in order to have a similar number of analyzed samples, but also because the city of Cluj Napoca has recorded the highest concentrations of THMs during this period (September 2009-February 2010).

The results showed that for all three investigated places, the characterization of cancer risk exposure to chloroform showed that the risk of cancer in a 25 years exposure is predominantly by inhalation (E-05), followed by the risk of ingestion (E-06) and by skin contact (E-07). In Cluj Napoca inhalation exposure is responsible for the increased cancer risk for chloroform, for a period of 25 and 35 years of exposure (4.27 E-05 5.98 E-05 respectively), followed by the risk associated with ingestion (2.70 3.78 E-06 and E-06) and dermal (3.82 5.35 E-07 and E-07), the difference between ingestion risks and the one from inhalation is of one order of magnitude, as well as the dermal risk compared to the ingestion risk (fig. 30).

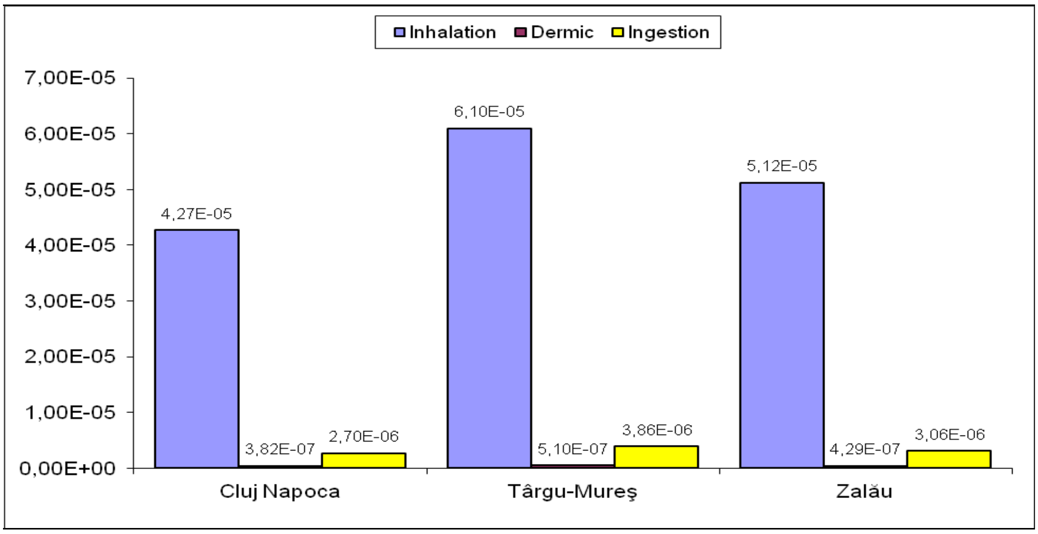


Figure 30. Cancer risk average for chloroform exposure at 25 years in the three localities in the study

The same situation was highlighted for the cities of Târgu-Mureş and Zalău, where the cancer risks are higher for inhalation than for ingestion and dermal contact, but larger than in Cluj Napoca. Among the three studied localities there is a difference in the risk of cancer through inhalation, ingestion and dermal exposure, being statistically significant ($p \leq 0.05$) only between localities Târgu-Mureş and Cluj Napoca. In the case of inhalation exposure, an extra number of cases of cancer per 100,000 existing cases appears, ranging between 1.71 to 2.44 in Cluj Napoca and Târgu-Mureş (fig. 32).

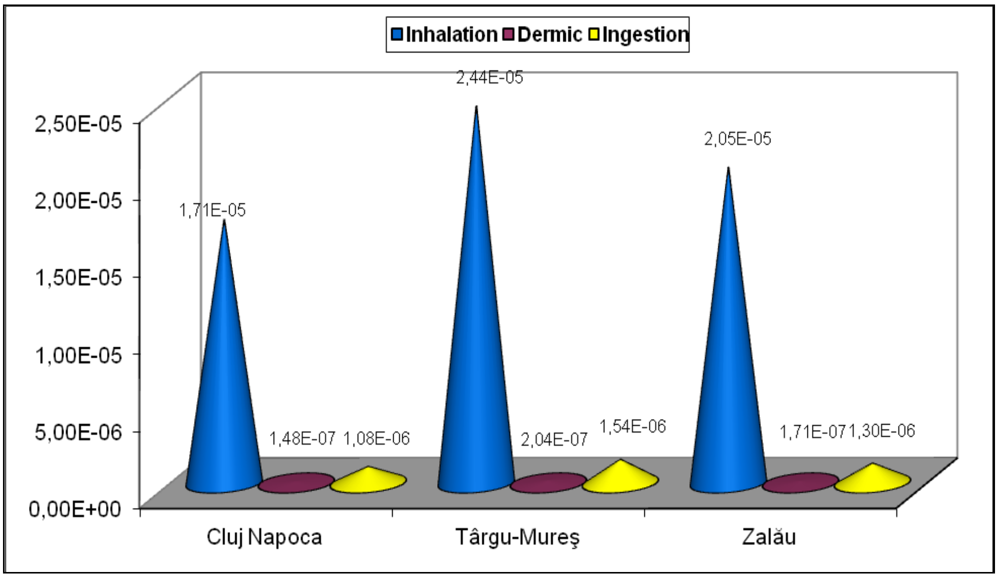


Figure 32. The difference between the risk of cancer average at 25 and 35 years of exposure to chloroform in the three localities in the study

Increasing the duration of exposure (from 25 to 35 years) increases the risk of cancer for all three routes of exposure.

According to the literature the risk of exposure E-06, E-07 can be considered negligible in the case of chloroform. Overall population in Târgu-Mureş is at significantly higher risk of cancer due to inhalation of chloroform, the number of cancer cases may grow to 6.1 cases per 100,000 existing cases and 3.86 cases per 1,000,000 existing cases. Inhalation contributes over 93% of the total cancer risk in all three localities, taking into account all three routes of exposure.

For an epidemiological study to have a high level of trust it is necessary to assess exposure at an advanced level, to understand the ways of penetration and the metabolism of chemicals in the body and the use of biomarkers of exposure. These biomarkers of exposure contribute to better study exposure assessment, augmenting the study in regards to its quality (Savitz, 2012).

5.4. Results of THMs concentrations biomonitoring in human urine under different conditions of exposure

Evaluation of the THMs and their species toxicity on the human body is made by assessing exposure via multiple routes of entry into the body (Lee et al., 2004). Chlorinated drinking water ingestion leads to digestion exposure of the population, and using tap water for personal hygiene and cooking increases the risk of accumulation of quantities of THMs in the body by inhalation and dermal contact (Jo et al., 2005).

Better studying of exposure assessment by biomonitoring of the total THMs species in urine was performed on a group of volunteer subjects, and showed that the only compound measured in the urine of the exposed subjects was chloroform with a concentration measured between 2.8 and 12.2 mg / l (table 27).

Table 27. Concentrations of THMs species in urine of investigated subjects

Participant ID	Chloroform $CHCl_3$ (μg/l urine)		Bromodichloromethane $CHCl_2Br$ (μg/l urine)		Dibromochloromethane $CHClBr_2$ (μg/l urine)	
	High exposure	Low exposure	High exposure	Low exposure	High exposure	Low exposure
01	2,8	3,5	<1	<1	<1	<1
02	6,9	6,3	<1	<1	<1	<1
03	3,4	4,8	<1	<1	<1	<1
04	7,1	5,3	<1	<1	<1	<1
05	3,2	3,2	<1	<1	<1	<1
06	4,2	5,1	<1	<1	<1	<1
07	5,8	2,8	<1	<1	<1	<1
08	3,5	5,4	<1	<1	<1	<1
09	12,2	5,6	<1	<1	<1	<1

Its identification in urine revealed that the frequency and duration of exposure can be more important than its concentration in the water. We have found higher concentrations of chloroform, bromodichloromethane and dibromchloromethane mostly in hot water than in cold water used by the subjects in the study, thus exposure is higher in hot water than in cold water (Table 28).

Table 28. Concentrations of THMs species identified in drinking water – cold and warm water

Chloroform $CHCl_3$ (µg/l)		Bromodichloromethane $CHCl_2Br$ (µg/l)		Dibromochloromethane $CHClBr_2$ (µg/l)	
Cold water	Warm water	Cold water	Warm water	Cold water	Warm water
40,5	44,3	7,7	7,6	3,5	3,0
45,0	46,8	7,6	7,4	<1	<1
43,0	46,5	7,5	7,4	<1	<1
50,0	50,4	8,1	8,2	<1	<1
53,8	53,0	7,8	7,9	<1	<1
11,8	12,9	7,7	9,3	5,3	6,3
50,0	51,2	7,4	7,6	<1	<1
50,0	47,7	7,1	7,4	<1	<1
50,9	50,2	7,3	7,5	<1	<1

The intake of chloroform by ingestion ranged from 0 mg / kg / day in subjects that do not consume any water from the distribution network, to 6.50E-04 mg / kg / day. The intake of chloroform by inhalation was one order of magnitude lower than the one calculated by ingestion, ranging between 1.33E-05 and 6.27E-05 mg / kg / day. For bromodichloromethane, intake by inhalation varied between 5.29E-06 and 7.53E-06 mg / kg / day, and for ingestion between 0 and 6.90E-06 mg / kg / day (Table 29).

Table 29. Chloroform and bromdichloromethane intake by ingestion, inhalation and dermal contact

Participant ID	**Oral ingestion** (mg/kg/day)	**Inhalation dose** (mg/kg/day)	**Dermal contact** (mg/kg/day)	**Oral ingestion** (mg/kg/day)	**Inhalation dose** (mg/kg/day)	**Dermal contact** (mg/kg/day)
	Chloroform			**Bromodichloromethane**		
01	2.50E-04	5.19E-05	7.58E-05	4.83E-05	6.71E-06	4.94E-05
02	2.90E-04	4.51E-05	7.87E-05	4.99E-05	5.38E-06	5.13E-05
03	3.90E-04	6.27E-05	8.66E-05	6.90E-05	7.53E-06	5.64E-05
04	0	4.57E-05	8.46E-05	0	5.60E-06	5.51E-05
05	0	4.71E-05	7.91E-05	0	5.29E-06	5.15E-05
06	6.50E-04	1.33E-05	3.42E-05	4.25E-05	7.23E-06	2.23E-05
07	2.00E-05	6.09E-05	9.38E-05	3.00E-05	6.82E-06	6.11E-05
08	0	5.27E-05	8.20E-05	0	6.16E-06	5.34E-05
09	8.40E-04	6.10E-05	9.59E-05	1.20E-05	6.87E-06	6.25E-05

The route of exposure is decisive in terms of daily intake of THMs in drinking water, for the subjects in study, this being related with ingestion, and then with inhalation for chloroform or dermal contact for bromodichloromethane. The presence of different concentrations of THMs in urine may be linked with the fact that individual metabolism characteristics and elimination of THMs are specific to each organism.

6. Case study - groundwater source

Case studies have an important value in terms of processing a large volume of data. Such studies are essential to observe the extent to which some general characteristics are retrieved in particular situations.

Our case study was conducted in Slobozia, Ialomita county, between 2009 -2011. The phases of the study were the following:

- Receiving data from the water company regarding water quality during 2009 – 2010,
- Questionnaire-based study on water consumption and habits related to it – 2010,
- Analysis of the concentration of THMs in the distribution network – 2011,
- Dose calculation and daily intake of THMs for cancer risk.

The water treatment plant in Slobozia, Ialomita County, provided drinking water in 2010 to about 70,000 residents from the localities Slobozia, Slobozia Nouă, Amara and Ciulnița. The water source comprised 20 wells, with a maximum depth of 110 meters, located on a N - S alignment on road DN 21 Slobozia-Călăraşi on the way from Slobozia to Călăraşi, between Km 92 and Km 105 milestones.

The deep water source which provides raw water for the centralized water system in Slobozia is characterized by elevated levels of the following compounds: ammonia, sodium, iron and manganese, each with significant oscillations. Chlorination is performed at high levels during the treatment process due to the existence of ammonia ions, which recommended such treatment technique, the other parameters analyzed (oxidability and nitrogen cycle) fall within the maximum allowed limits.

In terms of quality, we interpreted the results for the physicochemical analyses of the water from wells during 2009 (from putting into service) and 2010. In July 2009 - May 2010 water quality from the drainage basin was analyzed in 12 sampling sessions for wells 0-17 and 3 sampling sessions for the 18-19 wells (only in 2010, undergoing technological tests). Water analysis was performed for the parameters included in Act 458 (rl) / 2002, totaling 53 tests / water sample.

The test results have shown that oxidability increases in the distribution network compared to the exit point of the treatment plant. Due to high levels of chlorination and the existence of a growing nitrogenous organic matter in the network it leads to favorable conditions for generating THMs, whilst the increasing concentration of THMs and total THMs is due to increased concentrations of tribromomethane and dibromochloromethane at some points in the network (Table 30, Table 31).

Table 30. The average of physico-chemical results (selective) in samples from 2009-2010 – exit water treatment plant

30.06.2009 -24.06.2010	pH unit.	Oxidab. mgO2/l	Ammonia mg/l	Nitrates mg/l	Nitrites mg/l	Iron mg/l	Free chlorine mg/l	Bound chlorine mg/l
No.of determinations	597	597	592	222	99	354	285	282
Average	7.54	1.44	0.0476	0.0018	2.41	0.112	0.78	0.87
Nr.of exceedings	0	0	0	0	0	0	281	0
% exceedings	0	0	0	0	0	0	98.6	0

Table 31. The average of physico-chemical results (selective) in samples from 2009-2010 – distribution network

30.06.200921. 06.2010	pH unit .	Nitrites mg/l	Nitrates mg/l	Ammonia mg/l	Iron mg/l	Oxidab. mgO/l	Free chlorine mg/l	Total chlorine mg/l
No.of determinations	102 0	512	884	996	993	914	1050	1048
Average	7.4 7	0.36	0.004	0.021	0.34	1.75	0.135	0.192
Nr.of exceedings	0	0	0	0	528	0		
% exceedings	0	0	0	0	52.6	0		

One third of the total concentration of THMs is represented by chloroform and bromodichloromethane (fig. 43) - classified as carcinogens, and the remaining 70% are the brominated forms (dibromclormethane and tribromomethane), which are not classified as human carcinogens, although it was demonstrated to cause tumors in laboratory animals (IARC, 1991).

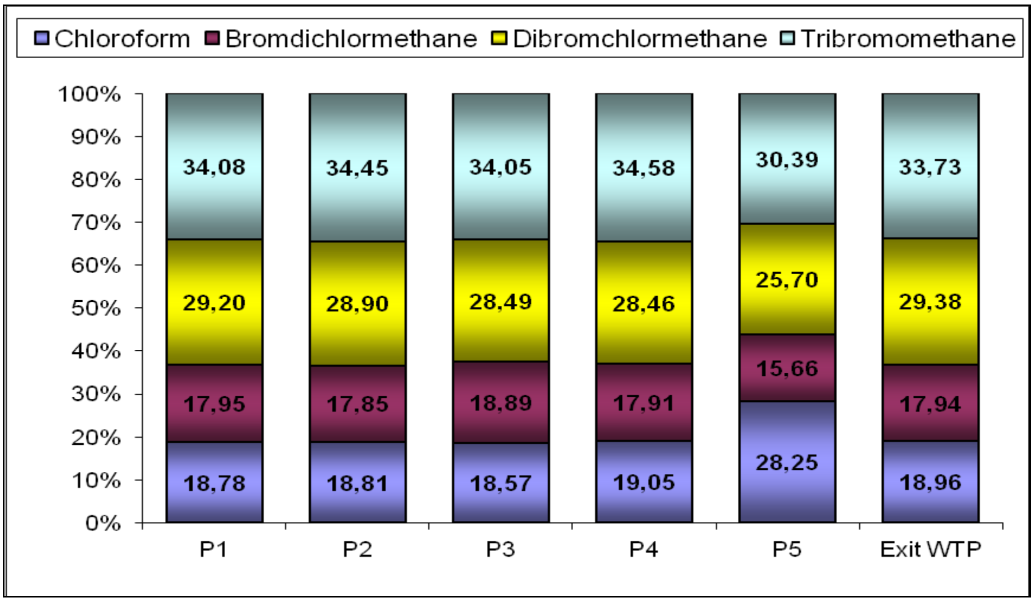


Figure 43. THMs species from drinking water (%) – 31.01.2011

There is an increasing trend in the concentration of total THMs and compounds in the network, the increase of the total concentration of THMs is due to increased concentration of bromodichloromethane and dibromchloromethane that continue to form in the distribution network. All prior measurements for the drinking water distribution network (data received from the Company) only showed concentrations of total THMs, without their speciation, so we cannot say with certainty whether tribromomethane or dibromochloromethane concentrations are specific circumstances for the sampling time or if this is a recurring situation.

6.1. Questionnaire-based investigation of residents in relation to consumption of tap water

During July 2010 a number of 102 persons were investigated based on a questionnaire, who were consumers of drinking water provided by the water treatment plant in Slobozia.

The questionnaire applied to a group of people supplied with water from the centralized water system in Slobozia, revealed that most of them do not use tap water for drinking, and more than that, it is not used either for cooking or preparing beverages. It should be noted that only 16.1% of the respondents drink water from the distribution network, most people using bottled water for this purpose, namely 74.2%, the remaining 6.5% drink water from wells. There are also subjects using both network and bottled water (9.7%) for drinking or associate with the same purpose, bottled water with well water (6.5%), while 3.2% use drinking water from the network and from wells (fig. 36).

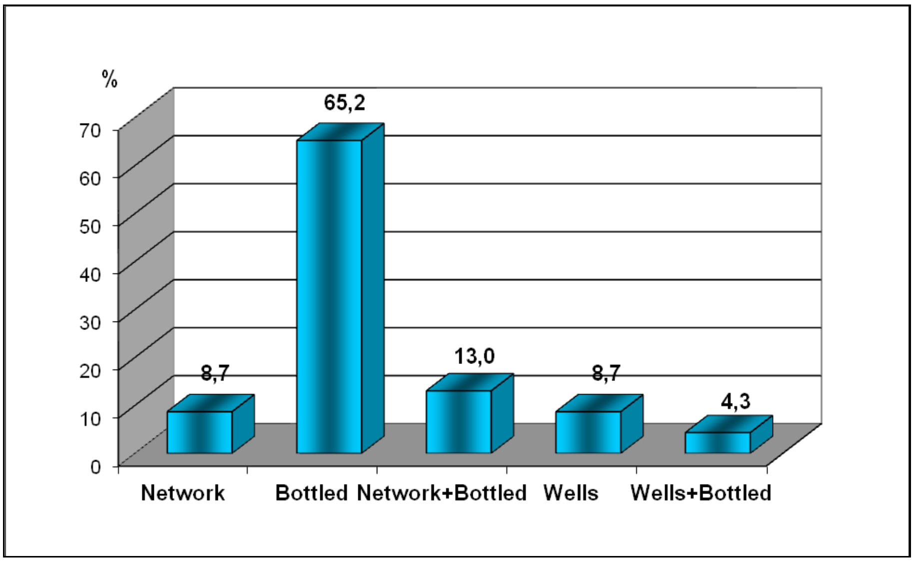


Figure 36. Types of water used for drinking (detailed)

Using water from the network exclusively for purposes other than human consumption through daily drinking water is recognized by 64.6% of respondents: either for cooking and other domestic purposes (cleaning, hygiene, etc.) - 32.3% or strictly only for domestic purposes - 32,3% (Figure 37).

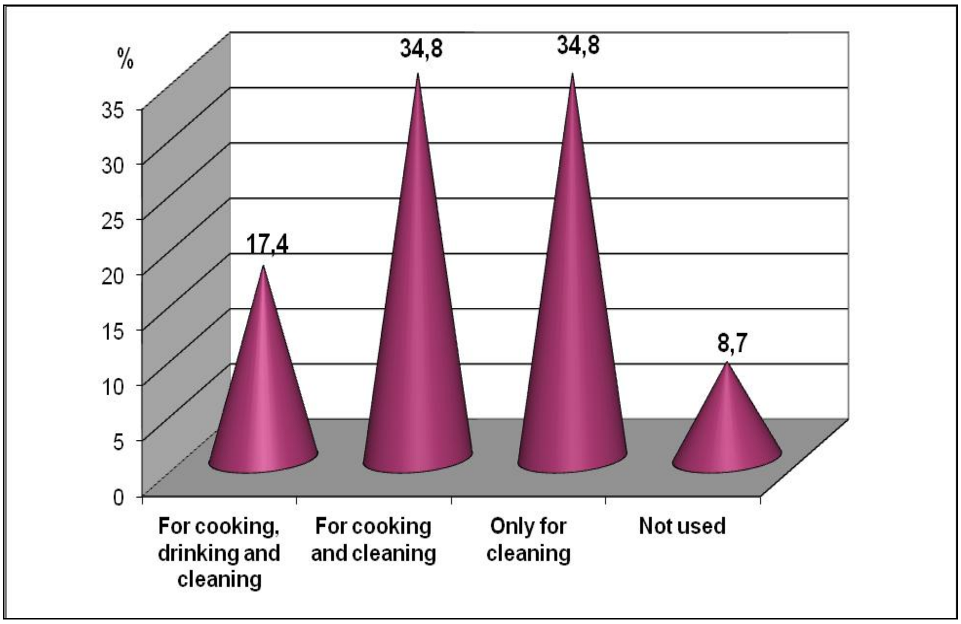


Figure 37. Use of tap water for drinking and other purposes

By interpreting the responses to the questionnaire it was noted that 77.4% of respondents believe that water has an unpleasant appearance having a yellowish coloration and 16.1% of subjects also observed the presence of suspensions. Unpleasant taste and smell of mud or sewer is perceived by 30% of respondents and 12.9% declare that the network water has metallic odor and taste (of iron). A number of respondents (6.5%) have even noticed the presence of chlorine taste (Table 34). All this explains why the network water is less used for drinking and cooking.

Table 34. Special organoleptic characteristics of tap water

Tap water		%
Why tap water is not used	Poor quality	24,0
	Colour (yellow-reddish)	56,0
	Suspensions	16,0
	Bad taste	24,0
Aspect	Colorless	16,1
	Colour (yellow-reddish)	77,4
	Suspensions	16,1
Smell	Odorless	48,4
	Unpleasant (stale, mud, sewer)	38,7
	Metal (Fe, rust)	12,9
Taste	Tasteless	48,4
	Unpleasant (stale, mud, sewer)	32,3
	Metal (Fe, rust)	12,9
	Chlorine	6,5

The particularities given by the organoleptic characteristics lead to water use especially for personal hygiene (shower, bath), so that the main routes of exposure of the population to THMs are by inhalation and dermal contact.

6.2. Cancer risk in exposure to THMs in drinking water

Cancer risk calculations were carried out for the concentrations of chloroform, bromodichloromethane and tribromomethane identified in five points in the distribution network on 31/01/2011, for adults (standard weight 70 kg) through inhalation and dermal contact, for an exposure interval ranging between 25 and 35 years.

The risk of cancer calculations at 25 or 35 years for the 3 species of THMs considered, show that for the dose of exposure and the daily-calculated intake, inhalation exposure is higher than through dermal contact, for adults. The risk of exposure is greatest in chloroform, followed by bromodichloromethane and tribromomethane, both for inhalation and skin contact (Fig. 44, 45). Considering a 25-year exposure in adults, it is likely to limit the temporal exposure.

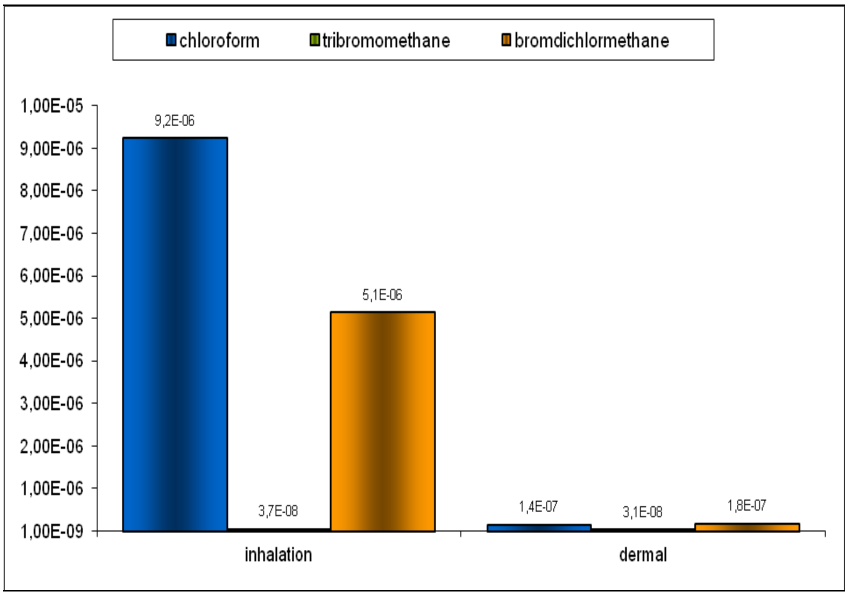


Figure 44. Cancer risk for adults at 25 years of exposure, calculated for the three species of THMs

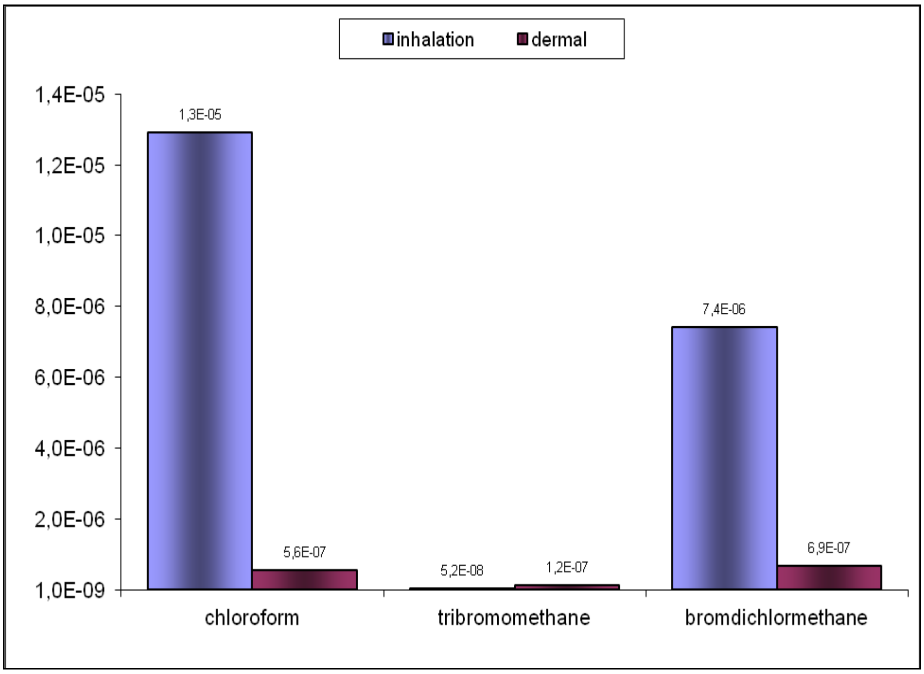


Figure 45. Cancer risk for adults at 35 years of exposure, calculated for the three species of THMs

The results showed that through inhalation / dermal exposure to concentrations of chloroform, bromodichloromethane and tribromomethane, a daily intake dose and an exposure dose resulted, corresponding to a risk of developing cancer ranging from 1.46 cases per 100,000 existing cases to 9.52 per 100,000,000 cases of pre-existing cases in adults for a period of 25 years of exposure. In the case of 35 years of exposure, the risk of cancer is maintained at approximately the same values as for 25 years of exposure, in the case of exposure to chloroform, bromodichloromethane and tribromomethane, for adults.

Self-restraining of water consumption of the population does not reduce the risk of cancer associated to THMs (chloroform and tribromomethane), inhalation exposure being decisive in regards to the dose and the daily intake of the compound in question.

For the investigated locality it is not necessary to change the water source, but to adjust and rehabilitate the treatment process and the distribution network. The lack of the re-chlorination at storage tanks level reduces the risk of THMs generation in the water distribution network, thereby decreasing the population exposure to THMs.

General conclusions

• European Community policy on health and safety of the population in relation to drinking water is a priority at present,

• Together with the lack of data from Romania on the effects on health outcomes regarding exposure to different concentrations of THMs in water, I can align the chosen research topic with current trends and show its importance in the development of strategies on the water-health relationship,

• The choice of the study area was based on previous knowledge on centralized water supplies of large urban agglomerations in Transylvania, with and without quality aspects of water that might constitute potential health hazards for consumers,

• Exposure assessment model was developed based on direct measurements of the concentrations of THMs and their species in water, and showed it is suitable for the intended purpose,

• The quality of the investigated water sources (surface sources - reservoirs and one river), was more or less variable during the study, and it was an important parameter in the water treatment equation and of the change of the treatment process over time,

• Even if the water treatment plants in study Gilău, Vârşolţ, Târgu-Mureş, are using conventional methods (coagulation, settling, filtration and disinfection with chlorine), changing the water source quality imposed adjustment of the treatment methods by adding or excluding steps,

• Pre-chlorination like any pre-treatment corrects raw water by oxidation, and when using chlorine compounds, it should be followed by a step of reduction of the secondary disinfection compounds before the final disinfection,

• Assessment of THMs precursors in both raw water and distribution network showed that the main place for THMs generation is the latter (distribution network), as highlighted in our research by exceedings of the maximum allowable concentration for total THMs in network water in two of the investigated localities (Zalău, Târgu-Mureş),

• The predominant species identified in the highest concentrations in all analyzed water samples for treated water from surface sources was chloroform, a substance classified by IARC in group 2B, possibly carcinogenic, and included on the list of priority hazardous substances of the European Community,

• Overall the presence of THMs species was not identified constantly in all localities and in all water samples,

• Higher levels of THMs in the distribution system were mainly influenced by re-chlorination at the storage tanks level, along with the presence of organic nitrogenous matter within the water distribution pipes,

• Regarding the studied compounds, the effects upon health are conditioned by intensity, frequency and duration of exposure,

• Frequency and duration of exposure to THMs in drinking water of the population in the three cities studied, was determined by questionnaire-based investigation of a numerical representative populational sample for each city (total of 629 persons) who provided information about the habits related to water consumption and its use for different purposes,

• As expected, consumption of water from the public network was significantly differentiated by age, sex, place of residence, level of education and place of use (home or workplace)

• Interviewing the persons revealed that in terms of quantity, the water consumption from the distribution network is limited or very limited, being replaced by bottled water as a general trend,

• Many of the subjects motivated the limited water consumption by the poor organoleptic properties of water,

• Based on questionnaire data, we determined that the main route of exposure to THMs is not drinking water, but the other ways of using it, for personal hygiene (bath / shower), respectively,

• Using the ATSDR calculation model for the dose, daily intake and cancer risk, we could assess this type of specific and severe effects in exposure to different species of THMs,

• Considering that the main exposure route highlighted after the application of questionnaires was inhalation, the ATSDR calculation model was modified and customized to calculate the risk of cancer following the use of the shower,

• The secondary route of exposure to THMs associated to personal hygiene became the dermal route, hence the same ATSDR model was modified to calculate the cancer risk given by this type of exposure,

• Since the latency of cancer development is long-time, requiring a minimum of 20 years of exposure, scenarios for calculating risk in our study included only adults for an exposure duration of 25 and 35 years,

• Risk characterization in exposure to chloroform (classified in category 2B by IARC, potential carcinogenic) showed that the risk of cancer for a 25 years exposure is predominantly via inhalation (E-05), followed by the risk of ingestion (E-06) and dermal contact (E-07),

• According to the literature the risk of exposure for the orders of magnitude E-06, E-07 can be considered negligible in the case of chloroform,

• Due to elevated concentrations of THMs in water, the population of Târgu-Mureş is at significantly higher risk of cancer (although negligible, as mentioned), compared to the other two localities (Cluj Napoca and Zalău),

• As a whole, inhalation accounts for more than 93% of the total risk of cancer in all three localities, taking into account all three routes of exposure,

• The depth water source of the locality under study (Slobozia), although without or minimum bacteriological contamination, presented another water-contaminating parameter, namely ammonium, that requires chlorination at high levels for its reduction,

• The existence of a state of advanced degradation due to the considerable age of the distribution network leads to the identification of indicator parameters (oxidability) increasing in the water from the water distribution network compared to the water exiting the treatment plant,

• To confer microbiological safety, water is hyper-chlorinated at the treatment plant, providing favorable conditions for further generation of THMs in the distribution network,

• Compared to the other three localities investigated, with water originating from a surface area, the main compounds identified in the distribution network were dibromochloromethane and tribromomethane,
• Investigation based on the same questionnaire on habits regarding consumption and use of water from the public network in this locality also showed that a small number of the population consumes water for drinking, not using it for cooking or for preparing beverages,
• The reason for rejecting water is given by its altered organoleptic characteristics due to the presence of iron and manganese in excess,
• The primary routes of exposure to THMs remain inhalation and the dermal route,
• Cancer risk was calculated for chloroform and bromodichloromethane for inhalation and dermal contact because they are classified as having carcinogenic side effects,
• Cancer risk was calculated for tribromomethane, even if IARC currently lacks the evidence to classify this compound as a potential carcinogenic, although there is evidence of carcinogenicity in laboratory animals,
• Cancer risk exposure to these compounds ranged from 9.52 additional cases for 100 million of existing cases and 1.46 additional cases for 10,000 existing cases (for tribromomethane),
• Although for the 4 localities studied (Cluj Napoca, Zalău, Târgu-Mureş and Slobozia) the primary route of exposure was found to be inhalation, followed by the dermal route, concentrations of a particular compound in drinking water was the main cause for the risk of exposure for each town's population,
• By far, the population in Târgu-Mureş is at higher risk of cancer through inhalation and dermal contact, due to the compound chloroform,
• Slobozia is in first place regarding tribromomethane and dibromchlormethane, because it is the place where the highest concentrations were identified,
• Under these conditions the population in Slobozia is exposed to dibromchlormethane by ingestion,
• Multiple exposure resulted in the highest calculated cancer risk, for the population of Târgu-Mureş, for all compounds investigated,
• In the case of the 35 years duration, the risk of cancer increases compared to the risk calculated for the 25 years period, and limiting the consumption of drinking water does not reduce the overall risk of cancer,
• As a result of exposure to various concentrations of THMs, the presence of THMs in human urine as biomarker of exposure was identified in a group of volunteers,
• The presence of different concentrations of THMs in urine can be attributed to individual characteristics regarding the use of water as well as those regarding metabolism and elimination that are specific to each organism,
• The results of the study show that integrating information from the environmental, economic and social data, accompanied by promotion of specific technical measures and generating sanogenous behaviors, is the basis for appropriate policies for the health and environmental

protection in an integrated system in order to maintain the accepted risk for population exposure to THMs in drinking water,

• Research on the action of chemical compounds in water have led in time to modification of the quality standards, while "safe water" definition according to the quality criteria is likely that in the coming years to be a notion that will be updated also from the point of view of trihalomethanes as byproducts of water disinfection.

Originality and innovative contributions of the thesis

• Our study is **a novelty at national level** because it brings together a **comprehensive assessment of exposure data** in order to **characterize risk** and health effects,

• The study showed **for the first time in Romania the presence of THMs in human urine and their variability associated to water consumption, our study being one of the few studies of its kind worldwide,**

• The results of this research aggregate **a comprehensive database** on **exposure to THMs at receptor level** in three major urban areas of Transylvania,

• Questionnaire-based study on **water consumption habits** conducted for the first time in Romania on **representative samples** of urban areas in the study, showed the general trend of **limiting the consumption of drinking water from the distribution network,**

• We also managed to singularize the system and to calculate **for the first time in Romania the cancer risk for the exposure to THMs associated with different exposure durations.**

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