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EXPOSURE ASSESSMENT TO TRIHALOMETHANES FROM THE EPIDEMIOLOGICAL PERSPECTIVES

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Abstract: On a global scale, pathogenic contamination of drinking water poses the most significant health risk to humans. In order to meet the drinking water criteria the classic water treatment processes include: coagulation/decantation, filtration and disinfection. Chlorination is the most widely used technique for disinfection of drinking water, it determines the formation of chlorination by-products such as halogenated trihalomethane which depend strongly on the composition of the natural organic matter in the raw water, pH, temperature, chlorine dose, reaction time, or diferent other factors from the pipe environment (specific material from the pipe wall, biofilm, bioactivity of bacterial growth in biofilm). The trihalomethanes have negative effects on human health like genotoxicity and carcinogenicity.

Key words: drinking water, disinfection by chlorine, organic pollution, trihalomethanes, health effects

1. INTRODUCTION

Disinfection by chlorination is the most important step in the water treatment for public supply, as chlorine remains in the water as it is not consumed. It is the most widely used cost-effective method of disinfection practiced worldwide and has lead to the successful control of waterborne diseases for more than a century. Identification of chlorination by-products (CBPs) and their potential health hazards has created a major issue in balancing chemical toxicity with risks from pathogenic microbes.

Trihalomethanes (THMs) are a class of disinfection by-products formed when chlorine reacts with the natural organic matter. The THMs consists of four compounds: Chloroform (CHCl3), Bromoform (CHBr3), Dichlorobromomethane (CHCl2Br) and Dibromochloromethane (CHClBr2). The limits of total THMs in public water supplies are 100 µg/l Romania (EU) and 80 µg/l in the USA (US Environmental Protection Agency).

The humans are exposed to THMs through ingestion (drinking water), inhalation (vapors released from water into indoor air) and skin (during showering and bathing).

Basically, the THMs exposure can conduct to non-carcinogenic and carcinogenic effects, the prevention of humans' exposure to THMs being more than necessary. The prevention includes the decreasing and monitoring of THMs in drinking water.

In order to reduce the public health risk from these toxic compounds, regulations must be enforced for the implementation of guideline values to lower the admitted concentrations or exposure.

2. METHODS

To better characterize the health risks posed to water consumers from the water treatment plants in Romania, we assess the risk of THMs exposure using the chemical analysis of THMs concentrations in water obtained directly from the water treatment plants (WTPs).

Drinking water samples were collected from different sampling points in the water treatment stations from Gilau, Targu Mures and Zalau and their corresponding distribution systems. These water treatment plants treat conventionally (coagulation, decantation, rapid filtration and disinfection by chlorine) surface water sources: Gilau reservoir, Varsolt reservoir and Mures River. Two WTPs use pre-chlorination as additional treatment step

according to the raw water quality (Varsolt-Zalau and Targu Mures). The water samples were collected three times (June-August 2009) and stored in 500 mL glass bottles. The water samples were stored at 4°C until analyzed after sodium thiosulfate ($Na_2S_2O_3$) was added to quench residual chlorine.

The water samples were analyzed for a series of indicator parameters for oxidizable organic matter content, chlorine (both precursors for THMs), total THMs and species (chloroform, dichlorobromomethane, dibromochloromethane and bromoform) using accredited/validated analytical methods such as: chemical oxygen demand – $KMnO_4$ (CCOMn) – titrimetric method (SR EN ISO 8467); nitrite (SR 3048-2), nitrate (SR ISO 7890-3) ammonium (SR ISO 7150-1/2001) - spectrometric method; free residual chlorine (Standard Methods 4500-Cl) and total chlorine (Standard Methods 4500-Cl) colorimetric test.

The trihalomethanes analysis was carried out by GC-2010 gas chromatography with electron capture detector (GC-ECD) and a Shimadzu AOC 5000 HSauto sampler. It was used the headspace technique. 10 mL of sample was filled into 20 mL headspace vials. They were shacked for 45 minutes at 60°C. A quantity of 2.5 mL from the gaseous phase was injected into GC. The results were read from the calibration curve, which was prepared using standard solutions of 0, 20, 40, 60, 80 and 100 µg/L each compound in Super Q water.

Databases were obtained by introducing water quality data in the Microsoft Excel version 5.0 program and processed statistically. Graphs were performed by the Microsoft Excel version 5.0 program.

3. RESULTS AND DISCUSSIONS

The values of the indicator parameters for pollution with oxidizable organic matter (precursor of THMs) and their evolution in the raw water entering the water treatment plant during the study period of 2009 are shown in table 1.

The clear and significant qualitative difference is observed between the water sources, the lowest organic load being recorded at the water source for Gilau water treatment plant (Gilau reservoir). Although these indicator parameters had low levels in all three sources, they presented significant variations, the most important increase being recorded in July, corresponding to a period of intense rainfall and high temperature. The highest average concentration of nitrates in the raw water from Tg. Mures WTP is specific to the rivers crossing localities and receiving tributary flow which also run through localities. A recent study conducted in the Mures County area (Hajdu et al. 2007) showed that the pollution sources (diffuse and punctual) from the localities effects the pollution of surface waters with nitrates.

Figure 1 shows on this line the situation of indicator parameters mentioned for the raw water from Gilau water treatment plant.

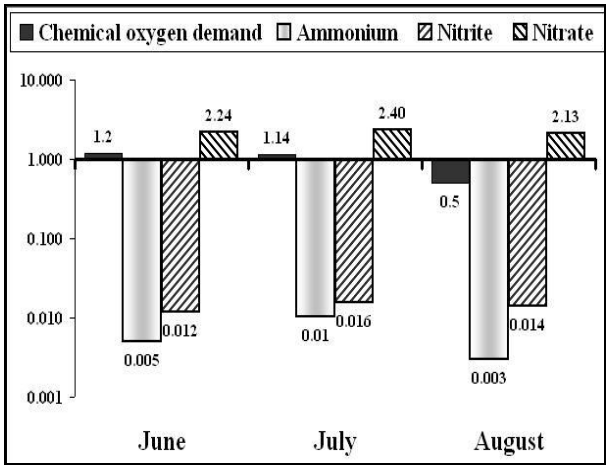

Figure 1. Levels of indicator parameters for the oxidizable organic matter in the water of Gilau reservoir.

Table 1. Levels of indicator parameters for the oxidizable organic matter in raw water at the water treatment plants

RAW WATER					
Locality		**Oxidability mg O/l**	**Ammonium mg NH_4/l**	**Nitrites mg NO_2/l**	**Nitrates mg NO_3/l**
Cluj	average	0,995	0,007	0,014	2,29
	st.dev.	0,33	0,004	0,003	0,14
Tg.Mures	average	2,25	0,056	0,116	2,56
	st.dev.	0,52	0,036	0,038	0,48
Zalau	average	2,24	0,073	0,049	0,13
	st.dev.	0,82	0,096	0,015	0,07

Raw water quality due to the oxidizable organic matter load and treatment process efficiency resulting in their significant reduction before chlorination is essential in controlling the formation of trihalomethanes. The formation of THMs and implicit chloroform is also influenced by the raw water composition as like the presence of natural organic substances (humic substances, microbial exudates and other dissolved materials originating from soil and terrestrial vegetation or from other aquatic biological processes) (Chan at al. 2002; Ristoiu et al. 2008, Nicolaou et al. 1993).

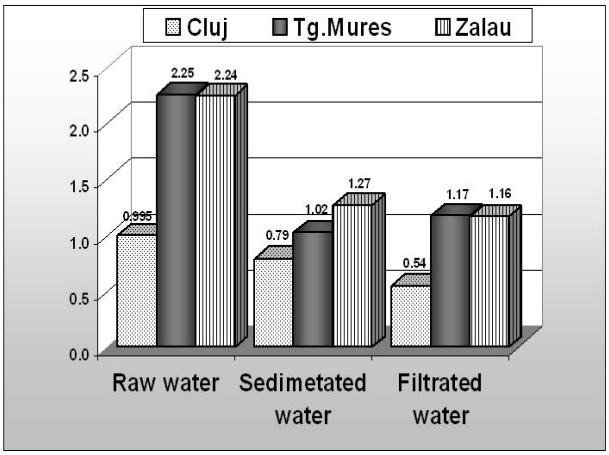

Figure 2. Average levels of oxidizable organic matter during the water treatment process.

Although the oxidizable organic matter recorded low levels in raw water, much below the maximum admitted limit in drinking water, reduction during the treatment was significant in all three water treatment plants and especially at Tg.Mures and Varsolt/Zalau water treatment plants where pre-chlorination of the raw water is used. (Fig. 2).

The lowest average values of the analyzed indicator parameters were measured in the water samples from the treatment process in Gilau WTS while the highest were measured in those from Varsolt/Zalau WTS, these results are closely correlated to the water quality at both water sources and to the efficiency of the treatment processes. Statistically significant differences ($p<0.05$) are observed as well as between the average concentration of nitrates in the water supplied by the three water treatment plants and with regard to the value of residual chlorine in the water from Cluj and Targu Mures (Table 2).

The quality of the water supplied for the population by the three drinking water suppliers met the requirements for use in potable purposes. Uniformly, the average values for the precursors of THMs in the treated water except for the free residual chlorine framed in the maximum admitted limits (Fig. 3).

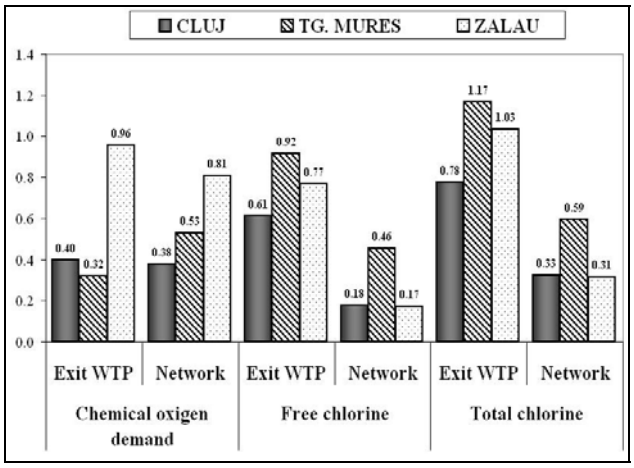

Figure 3. Average value for oxidability, free chlorine and total chlorine in the drinking water exiting the water treatment plant and in the distribution system (mg/l).

Table 2. Concentration of precursors of THMs in the treated water entering the distribution system 2009

WATER ENTERING THE DISTRIBUTION SYSTEM (EXIT WATER TREATMENT PLANT)							
Locality	**Parameters**	**Oxidability mg O/l**	**Ammonium mg NH_4/l**	**Nitrites mg NO_2/l**	**Nitrates mg NO_3/l**	**Free chlorine mg Cl_2/l**	**Total chlorine mg Cl_2/l**
Cluj	average	0,40	0,003	0,008	2,30	0,61	0,78
	st.dev.	0,24	0,000	0,004	0,28	0,09	0,05
Tg.Mures	average	0,32	0,003	0,005	2,71	0,92	1,17
	st.dev.	0,17	0,000	0,001	0,40	0,10	0,06
Zalau	average	0,96	0,003	0,009	0,36	0,77	1,03
	st.dev.	0,30	0,000	0,004	0,27	0,72	0,67

Referring to the maximum admitted levels for the free residual chlorine in the water exiting the water treatment plant/entering the distribution system (0.5 mg/L) we observed that the hyper-chlorination is practiced at all three water treatment plants, for the reason of maintaining the microbiological safety in the distribution system placed at distance and/or have a poor technical condition.

Figure 4 illustrates the change of the analyzed indicator parameters of the water in the distribution system in comparison with the water exiting the water treatment plant. Provided that the distribution system is a "living environment" and subject of aggressions from inside and outside, the water alters its quality, even if the parameter values frame within the potability limits. As a result similar or higher values are recorded for oxidability coupled with a decrease by consumption of the free residual chlorine and of the total chlorine afterwards. Furthermore, the general evolution of the analyzed parameters was similar at the three distribution systems and with regard to Ammonium concentration, nitrites and nitrates, respectively, they increased moderately (Fig. 4). Except for ammonium, there were differences in the average values of these parameters in the three drinking waters backed by their statistical significance for "t" and "p" values.

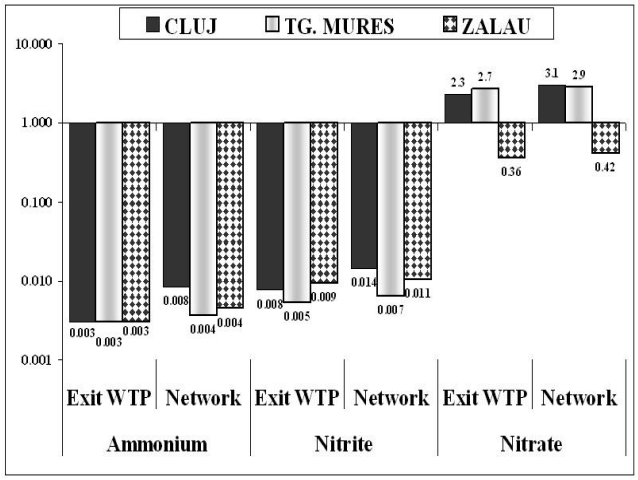

Figure 4. Average value for ammonium, nitrites and nitrates in the treated drinking water in the distribution system (mg/l).

The presence of an increased level of free residual chlorine in the treated water is an important factor of an enhanced genesis of disinfection by-products, even in conditions of low levels of oxidizable organic matter. As shown in Figure 5, if the water exiting the water treatment plant contains levels of free and total residual chlorine exceeding the admitted limits, the recommendation that the free residual chlorine level has to represent 80% of the total residual chlorine (for the disinfection to be efficient) is not achieved.

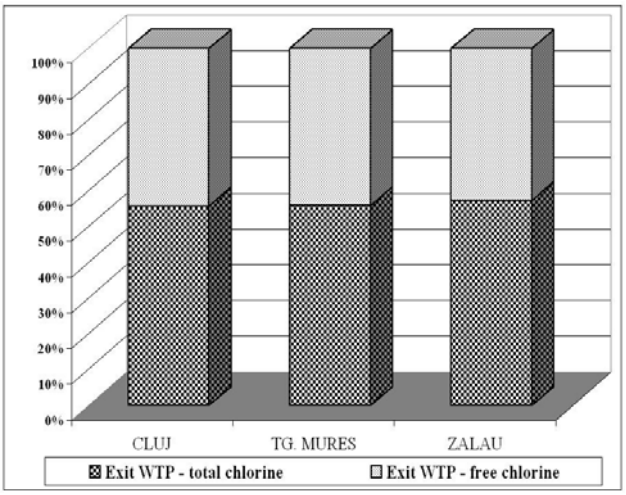

Figure 5. Chlorine levels in the drinking water exiting the water treatment plant

Moreover, this percent of free residual chlorine is even lower in the distribution system, indicating the formation of trihalomethanes. The altered quality of the water in the distribution system, as presented above supports this assertion (Fig. 6).

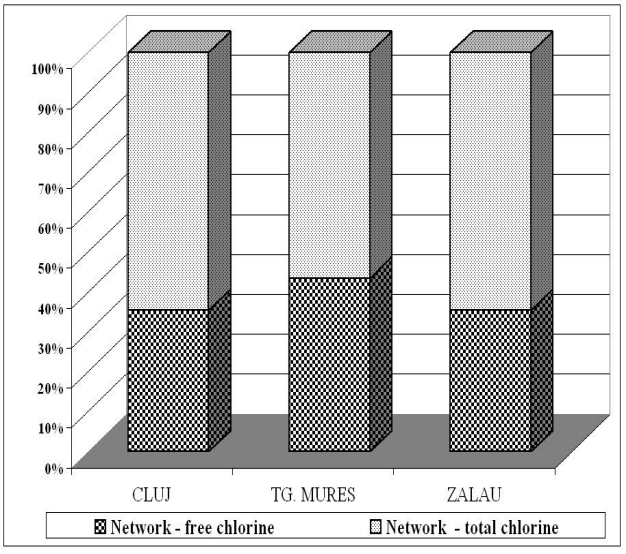

Figure 6. Chlorine levels in the drinking water distribution system

The concentration of trihalomethanes measured in the water exiting the water treatment plants showed average values between 39.69 and 74.88 µg/l. The highest average content of THMs was found in the treated water at Tg.Mures WTS (74.9 standard deviation 11.55 µg/l) correlating with

the residual chlorine content that also had the highest average value in this water category.

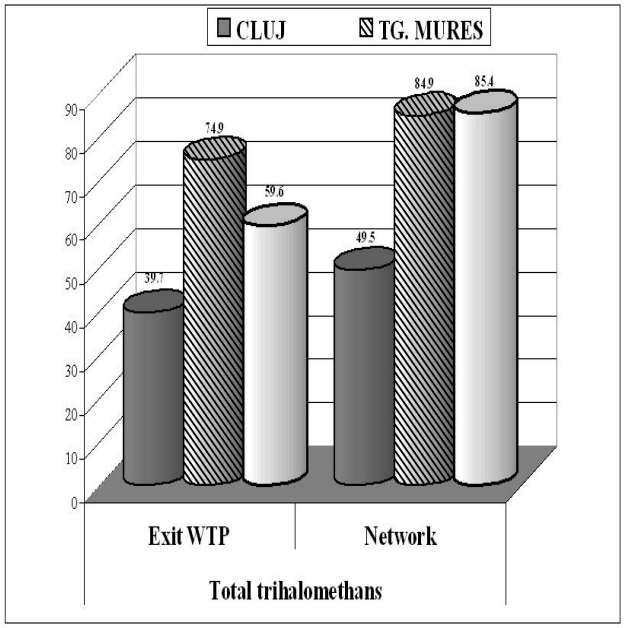

Figure 7. The average value of total THMs in the treated and supplied water (µg/L).

The concentration of THMs increased significantly in the distribution systems (Fig. 7) of the three cities, with average values between 49.53 and 85.39 µg/l, the highest average value being recorded in Zalau water distribution system. It is noted that the generation of THMs in Tg.Mures and Zalau distribution systems was significant mostly due to hyper-chlorination at Tg.Mures WTS, hyper-chlorination of water exiting Varsolt WTS, respectively and re-chlorination in Zalau distribution system. Differences between the levels of THMs in the distribution systems of Cluj-Napoca-Tg.Mures and Cluj-Napoca-Zalau were statistically significant for $p<0.001$ and $t=-5.34$.

Detailing the above-mentioned issues, the concentration of total THMs measured in the supplied water in Cluj-Napoca ranged between 27.78 - 81.1 µg/l. In contrast, in Targu Mures and Zalau, concentrations of total THMs were measured between 61.6-101.58 µg/l (2 out of 18 samples exceeded the maximum admitted concentration of 100 µg/l), and between 60.63-103.58 µg/l respectively (6 out of 17 samples exceeded the maximum admitted concentration of 100 µg/l).

Figure 8 shows the average concentrations of the four important compounds from the THMs group, both in the water exiting the water treatment plants and the water in the distribution systems of the investigated localities.

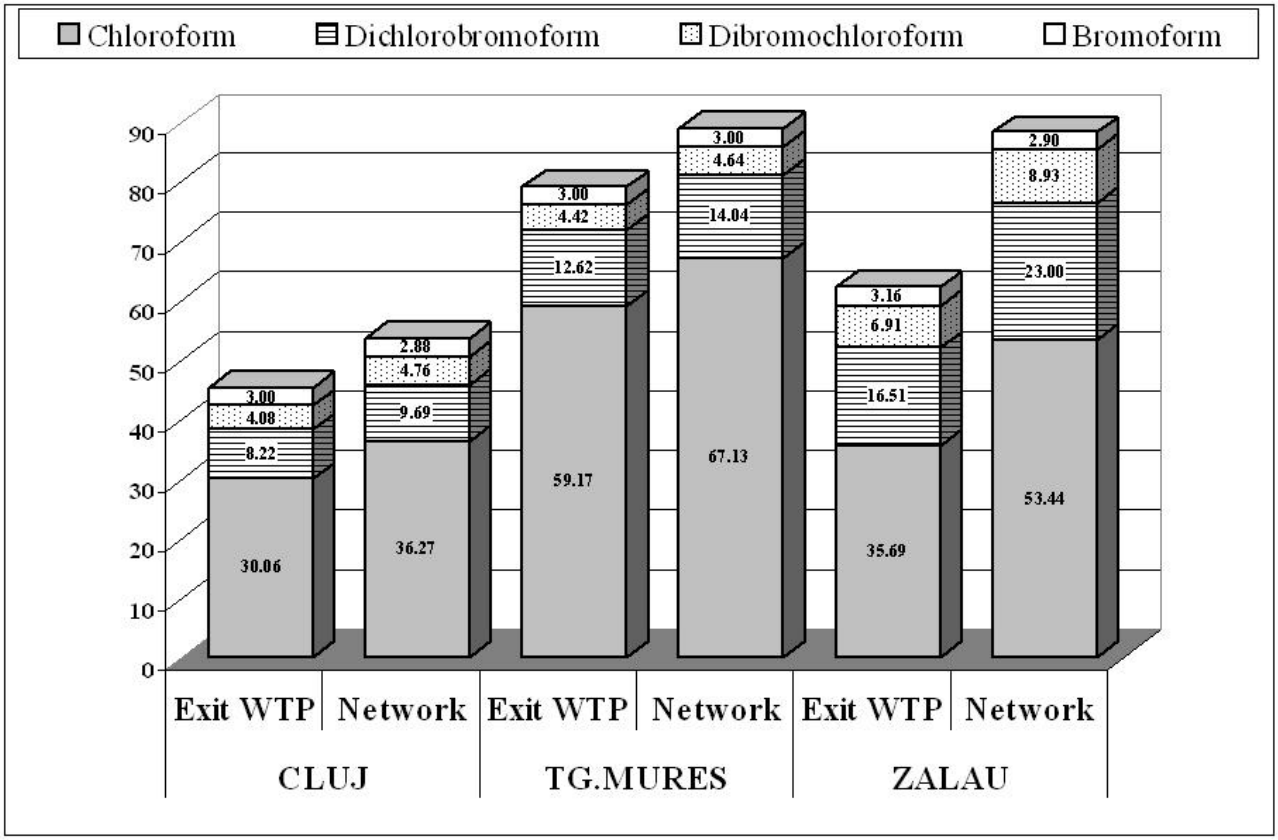

Figure 8. Species of THMs in the treated and supplied water (µg/L)

The main component, chloroform, is responsible for increasing the concentration of THMs in the distribution system in Cluj-Napoca and Tg.Mures, the latter recording the highest concentrations of chloroform (50.17-78.24 µg/l) out of the three cities. We mention once again that the highest values of residual chlorine were recorded in Tg.Mures distribution system. As a characteristic, a much higher concentration of dichlorobromomethane, dibromochloromethane and bromoform appears in the water exiting Varsolt/Zalau WTS in comparison with the other localities, due to bromates' content in the raw water (Varsolt reservoir).

The differences are statistically significant for dichlorobromomethane and dibromochloromethane between Cluj-Napoca-Tg.Mures and Tg.Mures-Zalau for $p<0.001$. It is notable that in Zalau city distribution system, besides the highest concentrations of total THMs to be recorded and samples that exceeded the maximum admitted concentration, the dibromochloromethane which is a compound frequently associated with carcinogenesis, also recorded the highest concentrations between 4-10.70 µg/l.The most important parameter involved in the dynamic generation THMs in an aqueous medium, is the concentration of residual chlorine, that varies according to other parameters such as emperature, pH or concentration of natural organic substances. Thus, typically high chlorine concentrations determine large amounts of chloroform. The relationship between the formation of THMs compounds (specifically chloroform) and chlorine was studied by laboratory kinetic experiments. The results demonstrated that the chlorine dose added directly and linearly in the water influences the rate of chloroform generation. A 2.5 mg/l chlorine dose increased the chloroform concentration (Chan 2002, Villanueva 2007).

A method to decrease THMs is to eliminate or reduce chlorination before filtration and to reduce organic matter. Decreasing the amount of high total organic carbon also decreases the high disinfection demand, as well as the formation of THMs.

In the drinking water networks the problem of balancing the need to maintain effective chlorination in the water and the effort to control THMs production still remain to be treated by the water suppliers. In Romania, as well as worldwide, water industry is currently replacing pipes with less reactive synthetic materials. Some studies (Chan at all 2002) showed that in this kind of pipes the biofilms form when microbial cells attach to the pipe surface and multiply, forming a slime layer in the pipe. The surface biofilm may impose certain impacts on the formation of THMs during distribution, contributing to the chloroform production. Both bacterial inactivation and THMs formation exert a chlorine demand and rely heavily on the natural organic matter (as a precursor for THMs formation and as a nutrient source for bacteria). It is known that the rechlorination significantly increases the THMs production. In some cases, the potential of rechlorination to prevent biofilm regrowth may be outweighed by its potential to pose a threat downstream on THMs control efforts.We obtained results showing that under the conditions of a low content of oxidizable organic matter in water and a level of free residual chlorine below 1 mg/l, the generation of THMs continues in the distribution system. From the health risk point of view the main threat to the water production is the maintaining the THMs levels low into the drinking water network. This presumes the permanent maintenance of the network and replacement of improper pipes.

Other major factors that participate in the process of THMs formation in the water distribution system is the bacterial attachment to surfaces and bioactivity of these organisms, including the microbial regeneration process and production of extracellular polysaccharides.It seems that chlorination acts selectively on bacteria, which explains their persistence and regeneration, while promoting additional formation of chloroform.

The decreasing of THMs in drinking water can be done also/and by some control measures at home (if anyone believes that this is an important factor in their lives) like filters, aeration or boiling of drinking water and using bottled water (Gopal et all 2007)

Toxicity of THMs occurs in those tissues that have the greatest ability to metabolize the THMs compound (e.g. chloroform). From the health effects' point of view dibromochloromethane and chloroform are the most important THMs compounds. Data on the non-cancer effects of THMs in humans are limited. These adverse effects in humans are similar to those observed in animals. There were describe effects on the central nervous system, liver damage, immunotoxicity (bromoform and dibromochloromethane), reproductive or developmental toxicity (chloroform) - secondary to maternal toxicity. The data on toxicity to the developing fetus (bromoform and dibromochloromethane) are inadequate to establish firm conclusions (Richardson et all 2007). There are no data from studies that are adequate to directly assess the potential carcinogenicity of chloroform

for humans. In animals, chloroform has been shown to cause increased incidence of liver and kidney tumors. This carcinogenic response occurs only at high dose levels that result in cytotoxicity. Chloroform is not a strong mutagen and is not likely to cause cancer through a genotoxic mode of action. Carcinogenic effects have been observed in animals exposed to bromoform and dibromochloromethane. Chronic oral exposure to bromoform resulted in increases in the occurrence of intestinal tumors in female rats. Dibromochloromethane induced liver tumors in male and female mice (Villanueva et all 2007).

Recent studies associated the exposure to trihalomethanes with increased risk of bladder and rectal cancer (colorectal cancer). Among the THMs compounds, dibromochloroform was the most closely associated with cancer risk, (0.6 μg/l to cause a one in one million cancer risk increase) followed in order by bromoform, chloroform and dichlorobromoform.(Nieuwenhuijsen et all 2000).

Under the Proposed Guidelines for Carcinogen Risk Assessment (U.S. EPA, 1996a, U.S. EPA, 1999), chloroform is *likely to be carcinogenic to humans by all routes of exposure* under high-dose conditions that lead to cytotoxicity and regenerative hyperplasia in susceptible tissues (U.S. EPA, 1998c,d). The International Agency for Research on Cancer (IARC) classified chloroform as a possibly carcinogenic to humans, group 2B (Backer et all 2000). The International Agency for Research on Cancer (IARC) classified bromoform as a probable human carcinogen, group 2B and dibromochloromethane as a possible human carcinogen, group C. Taking into account this classification the prevention of humans' exposure to THMs is more than necessary. The prevention includes the decreasing and monitoring of THMs in drinking water (Egorov et all 2003).

Drinking water contamination by chloroform is recognized as an alarming public health problem that may be responsible for diseases such as bladder cancer and other conditions including cardiac anomalies, stillbirth, miscarriage and pre-term delivery (Nieuwenhuijsen et all 2000). In order to better characterize the link between THMs exposure and health outcomes, disease risk must be evaluated in terms of present and past exposure to pollutants, and the exposure sources must be analyzed in terms of their health impact (Nieuwenhuijsen et all 2000).

4. CONCLUSIONS

The water chlorination procedure, successfully used for the control of waterborne infectious diseases determines formation of chlorination by-products like halogenated trihalomethanes formed from the reaction of natural organic matter present in all types of water, with chlorine used as a disinfectant in the water treatment.

The total concentration of trihalomethanes and the formation of individual THM species in the chlorinated water strongly depend on the composition of the raw water and mainly the presence of natural organic matter in water, on operational parameters and chlorine dose, reaction time, and in the distribution system by the pipe environment created from the occurence of residual chlorine, and the bioactivity in biofilm. Generation of THMs takes place even at low concentrations of precursors, the level of the free residual chlorine influencing especially the formation and level of chloroform.

THMs toxicodinamics action mechanisms have negative effects on human health like genotoxicity, and carcinogenicity.

From epidemiological perspectives, exposure assessment to THMs in the three localities showed that the risk of occurrence of adverse effects (considering long-term exposure) exists, both when the measured concentrations of total THMs were high and mainly when some compounds that are mostly associated to carcinogenesis were identified at the same time.

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