CONCENTRATION OF TRIHALOMETHANES (THM) AND PRECURSORS IN DRINKING WATER WITHIN DISTRIBUTION NETWORKS

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ABSTRACT. Concentration of trihalomethanes (THM) and precursors in drinking water within distribution networks. Water chlorination is the disinfection method most widely used, having however the disadvantage of producing trihalomethanes (THM) as secondary compounds, which are included in the list of priority hazardous substances in water. THM formation is influenced by the raw water composition and chlorine from the disinfection process. This paper intends to highlight the individual values of the chemical compounds precursors of THM in the water network in order to correlate them with the evolution of THM concentration. The cities of Targu Mures and Zalau were chosen as the study area having surface waters with different degrees of contamination as the water source. Pre-treatment with potassium permanganate is used at the water treatment plant in Targu Mures, while pre-chlorination is used at the water treatment plant in Zalau. Water sampling was performed weekly between March-May, 2011 in three sampling points of each city, maintained during the period of study. Total THM and their compounds as well as THM precursors (oxidability, ammonium content, nitrites and nitrates) were measured. The water supplied in the distribution network corresponded integrally to the quality standards in terms of the analyzed indicators, including THM concentrations. The higher average THM concentrations in Zalau (52.01±14 μg/L) compared to Targu Mures (36.43±9.14 μg/L) were expected as a result of precursors concentration. In terms of THM compounds, they had similar proportions in the two localities, chloroform being clearly predominant, followed by dichlorobromoform and dibromochloroform, while bromoform was not identified. Statistical data analysis showed that the presence of THM precursors is correlated with the THM levels but not sufficient for their generation, even if they can be considered in general the basis of a valid prediction.

Keywords: drinking water, chlorination, precursors, THM.

1.INTRODUCTION

Drinking water is called generically water for human consumption. It is considered a "protected environment", drinking water quality being dependent on the raw water quality.

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Potability of water requires certain selected requirements in each case depending on the water source used, its composition and contaminants that require correction. Classically, the treatment processes include: coagulation/decantation, filtration and disinfection. To these technological steps, depending on the raw water quality a series of other additional processes can be added, such as pre-chlorination. During the disinfection process chlorine reacts with the natural organic matter in raw water, resulting in disinfection secondary compounds (DBP) such as trihalomethanes (THM) and haloacetic acids (HAA). Since Rook's pioneering work in 1974, it is known that chlorine used for drinking water disinfection purposes leads to the formation of many by-products potentially harmful to human health. (Gallard, von Gunten, 2002).

Trihalomethanes (THM) are a class of organic compounds. The four chemical species known as THMs are chloroform ($CHCl_3$), bromdichlormethane ($CHBrCl_2$), dibromchlormethane ($CHBr_2Cl$) si bromoform ($CHBr_3$) (Teskoy et al., 2008). In drinking water, the maximum allowed level for total THM (TTHMs) in the European Union is 100 μg/L, the maximum allowable values varying widely from one country to another (including the European Union Member States). In Austria, Switzerland and Luxembourg, the TTHMs regulatory limit in drinking water is 30, 25, 50 μg/L, respectively (Golfinopoulos, Nikolaou, 2005).

The most important parameter that occurs in the dynamics of THM generation in an aqueous environment is the chlorine concentration used, that varies depending on other parameters such as temperature, pH or concentration of natural organic substances (Ristoiu 2008, Ristoiu 2008, Ristoiu 2009). One of the important factors that influence the formation of chloroform and THM implicitly is the raw water composition, namely the presence of natural organic substances including humic substances, microbial exudates and other organic matters dissolved in waters of telluric and vegetal origin or coming from aquatic biological processes. Results from studies on natural organic substances in raw waters, disinfection and THM formation showed that there are many correlations between those and the chloroform level after chlorination (Krasner et al., 2006). Evaluation of THM precursors showed that THM generation is possible both at the treatment plant and also in the distribution network, especially where re-chlorination is applied. Precursors mean organic matter containing nitrogen, expressed by oxidability, and the amount of chlorine added to water during the disinfection process. The presence of DBPs in drinking water may lead to potential human health risks and many of the DBPs have been classified as probable or possible carcinogens (Hong et al., 2007).

This paper intends to highlight the individual values of the chemical compounds precursors of THM in the water network in two urban localities, in order to correlate them with the evolution of THM concentration.

2. MATERIAL AND METHODS

The localities chosen for the study were Targu Mures and Zalau. These cities have as drinking water source surface water bodies, but with different degrees of contamination that are treated for drinking purpose according to their quality. In Targu Mures chlorination is performed after water treatment by pre-oxidation, coagulation-decantation and filtration. Re-chlorination is not performed in the city water basins. In Zalau, the second locality chosen for the study, pre-chlorination, coagulation-decantation, filtration on sand layer and final disinfection with chlorine are performed.

Re-chlorination with gaseous chlorine is performed in city water basins. In order to measure the concentration of trihalomethanes and their species, water sampling was performed weekly between March-May, 2011 in three sampling points of each city, maintained during the period of study. Water samples were processed and analyzed in order to characterize the following parameters: oxidability, ammonium content, nitrites, nitrates, total THM and their compounds. Using standardized methods the following were analyzed: chemical oxygen demand by $KMnO_4$ method – tritrimetric method (SR EN ISO 8467:2001), nitrites (SR EN 26777:2002), nitrates (SR ISO 7890-3:2000), ammonium (SR ISO 7150-1:2001), free residual chlorine and total chlorine (Standard Methods 4500-Cl) by colorimetric test. Determination of THM concentration was performed by gas chromatography (Shimadzu GC Solution) with electron capture detector (GC-ECD). The analysis was performed using the headspace technique. Statistical data processing and graphics execution was performed using Microsoft Excel 5.0 program.

3. RESULTS AND DISSCUSSION

Table 1 shows the average values for oxidability, ammoniacal nitrogen, nitrites, nitrates and residual chlorine measured in the water network monitored weekly in the localities Targu Mures and Zalau between March-May, 2011.

Table 1. ***Precursors parameters values monitored between March-May 2011.***

Water network							
		Oxidability	**Ammoniacal nitrogen**	**Nitrites**	**Nitrates**	**Free chlorine**	**Total chlorine**
		mg O/L	**mg NH_4/L**	**mg NO_2/L**	**mg NO_3/L**	**mg Cl_2/L**	**mg Cl_2/L**
Tg.Mures	average	**0,68**	**0,005**	**0,014**	**4,10**	**0,17**	**0,35**
	st.dev.	**0,68**	**0,003**	**0,021**	**1,11**	**0,08**	**0,08**
Zalau	average	**1,18**	**0,006**	**0,010**	**2,25**	**0,11**	**0,28**
	dev.st	**0,81**	**0,009**	**0,015**	**0,92**	**0,05**	**0,07**

The average oxidability in Targu Mures ranked at a lower value than in Zalau, 0.68 compared to 1.18 mg/L. Ammoniacal nitrogen had similar average values in the two cities, with values of 0.005 mg/L in Targu Mures and 0.006 mg/L in Zalau. Nitrites in Targu Mures city water network were 0.014 mg/L, and 0.010 mg/L in Zalau. Instead nitrates had different values in the two localities, in Targu Mures their value reached 4.10 mg/L, and in Zalau the average value was 2.25 mg/L.

Although the oxidability values were higher in Zalau water network, free and total residual chlorine were higher in Targu Mures, which was probably dictated by the microbiological quality of water, and therefore the chance to generate THM in the distribution network can be higher in this locality (Fig.1, 2).

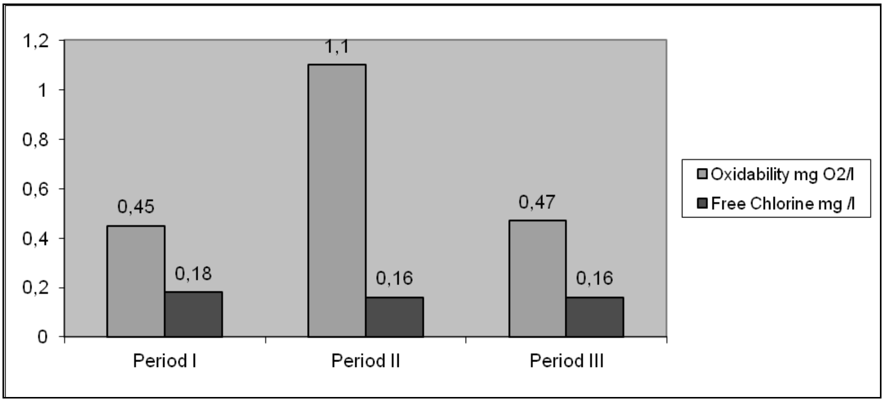

Fig. 1. ***Values of oxidability and free chlorine in Targu Mures.***

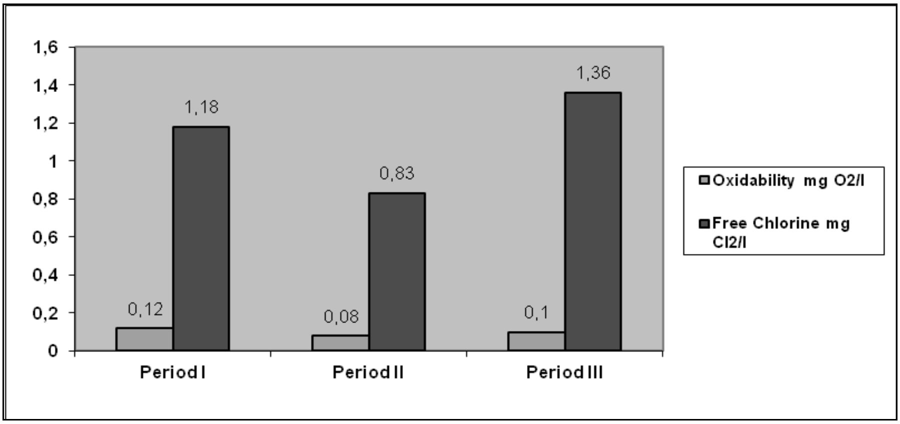

Fig. 2. ***Values of oxidability and free chlorine in Zalau.***

Nitrites and nitrates had higher concentrations in Targu Mures, even though the ammoniacal nitrogen was similar. Evolution of these indicators in Targu Mures water network is dictated by the raw water quality (Mures River) and by the treatment process (pre-treatment/chlorination). Oxidation of organic matter leads to nitrates/nitrites occurrence that in reaction with chlorine may generate high levels of residual chlorine bound and THM generation. Nitrates occurrence in surface water sources is reflected or not in the composition of the drinking water after treatment, and when present, the recorded values are generally low. In our study we identified low nitrates levels, the average in Targu Mures is 4.1 mg/L double in Zalau city (2.25 mg/L).

The concentrations of total THM and compounds in the water of the distribution network of the two monitored localities are presented in Table 2. The average for total THM is 36.43 μg/L in Targu Mures, average concentration lower than in Zalau city, where total THM ranks at the value of 52.01 μg/L, without exceeding the maximum allowable limit for the total THM concentration. Among the species of THM, chloroform prevail clearly in the water networks in both cities, with values of 27.25 μg/L for Targu Mures and 37.93 μg/L for Zalau. These values were expected due to the concentration of precursors (oxidability and total chlorine). We mention that the high levels of chlorine in Zalau distribution network is due to the re-chlorination in the water storage tanks of the city. Therefore the geneneration of THM is a continuous process in the distribution network, this process being influenced also by the rich nitrogenic organic matter from the pipes interior as well.

Dichlorobromoform and dibromochloroform have low concentrations recorded during the study, while bromoform concentration in the water samples analyzed was below the detection limit of the device.

Table 2. ***Average values for total THM and compounds.***

Water network						
		THM	**Chloroform**	**Dichlorobromoform**	**Dibromochloroform**	**Bromoform**
		μg/l	**μg/l**	**μg/l**	**μg/l**	**μg/l**
Tg.Mures	average	**36,43**	**27,25**	**7,10**	**1,39**	**-**
	st.dev.	**9,14**	**6,48**	**1,56**	**0,32**	**-**
Zalau	media	**52,01**	**37,93**	**11,22**	**3,08**	**-**
	dev.st	**14,00**	**11,82**	**2,24**	**0,62**	**-**

The parallelism between total THM and chloroform concentrations was clearly observed based on the individual values of the three THM species, during the 9 days of sampling both in Targu Mures and Zalau. In all analyzed samples, the level of chloroform is the highest, up to the value of 60 μg/L; in the mean time the concentration of dichlorobromoform follows with values between 5 and 15 μg/L in the water network. Bromine-containing species are situated at lower levels, between 1 μg/L and 3.58 μg/L.

The results obtained by analyzing the THM species are also confirmed by other studies. In Cluj-Napoca city, the presence of chloroform as the most common species of THM in the drinking water and having the highest concentration among the four species is an indicator for highlighting the THM formation in the water network (Ristoiu et al., 2009). Thach et al, (2012) shows in a study performed in 2009 that in analyzing trends from exposure to chloroform in these cities in Romania, it was found that there was a slightly significant association between chloroform levels and the distance of a sampling point from the point of chlorination in that network. Levels of THMs fell within an exposure range that some epidemiological studies have linked with increased risk of cancer, and some levels exceeded EPA and WHO-recommended exposure levels. Chloroform levels, on the other hand, were found to be generally lower than EPA-recommended exposure levels.

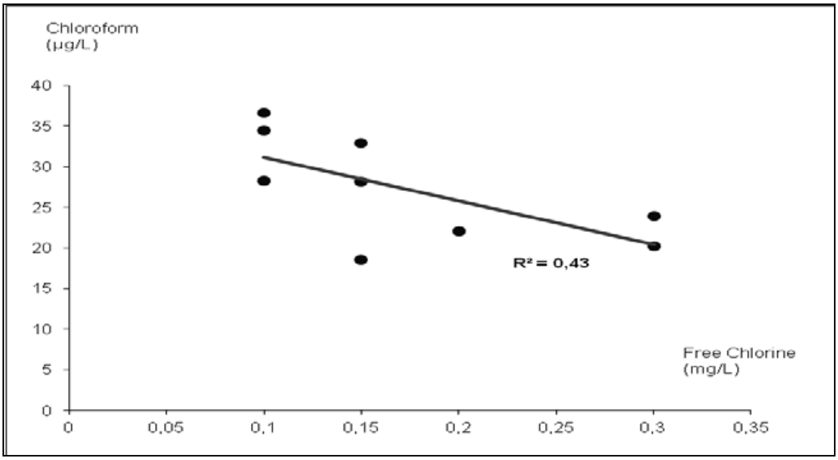

Fig. 3. ***Regression curve between chlororform and free chlorine in Targu Mures***

Considering the evolution of the THM concentration and precursors in the water network, we analyzed the correlation between the level of chloroform and the level of free chlorine in Targu Mures city and the level of oxidability with the total THM value for Zalau. In this context we applied the correlation method having as index the correlation coefficient (Pearson's *r*) to examine whether the upward trend of a value implies an upward trend, downward trend or no trend of the other. The ultimate goal is prediction, provided that it is possible, the two variables being indeed correlated.

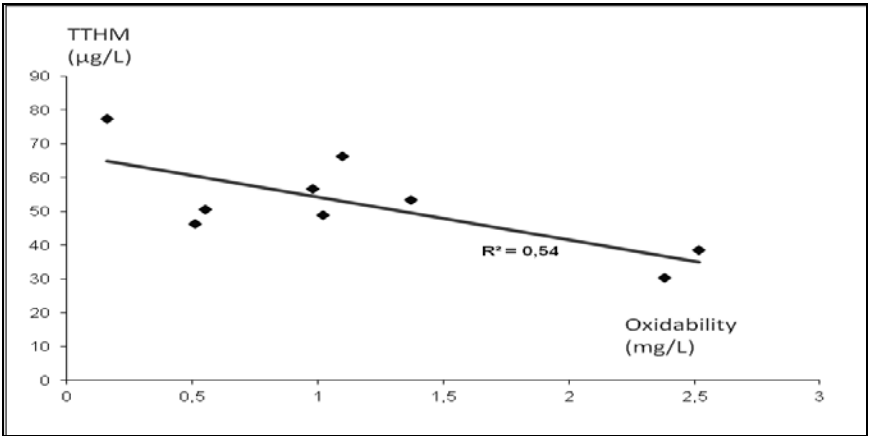

Fig. 4. ***Regression curve between oxidability and total THM in Zalau.***

Figure 3 shows an inverse correlation between the levels of free residual chlorine and chloroform. As much the chloroform level increases, the more the level of free chlorine in the water network decreases. For Zalau, Figure 4 shows that oxidability decreases and the total THM level increases, this being also an inverse correlation. Correlation index "r" shows a moderate positive association between oxidability, free residual chlorine and THM/chloroform, highlighting the manner and continuity of THM generation in the distribution network.

The presence of an increased level of free residual chlorine in treated waters is an important factor in the enhanced genesis of disinfection by-products, even under low levels of oxidable organic matter. Literature shows that there is an important relationship between the different species of THM and the amount of chlorine present in water. So the higher dose of chlorine added to the disinfection process, or along the distribution networks, the more high levels of chloroform concentration are recorded in the distribution network. Recent studies performed in Cluj-Napoca, Zalau and Targu Mures showed that the concentration of THMs increased significantly in the distribution systems of the cities, with average values between 49.53 and 85.39 μg/L, the highest average value being recorded in Zalau water distribution system. The study mentions that the generation of THMs in the distribution systems was significant mostly due to hyper-chlorination at WTS and re-chlorination. Differences between the levels of THMs in the distribution systems of Cluj-Napoca-Targu Mures and Cluj-Napoca-Zalau were statistically significant for $p<0.001$ and $t=-5.34$. The main component, chloroform, is responsible for increasing the concentration of THMs in the distribution system in Cluj-Napoca and Targu Mures. 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 (Gurzau et al., 2011).

From an epidemiological point of view, according to the experimental studies on animals, the risk of colorectal cancer and bladder cancer is associated with exposure to trihalomethanes. It is considered that to better characterize the relationship between exposure to THMs and health outcomes, the risk of disease 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 al., 2000).

4. CONCLUSIONS

In the studied localities the network drinking water meets the quality standards in terms of the analyzed indicators. The results show that THM precursors (free residual chlorine, nitrogenic organic matter) recorded different levels, the organic nitrogenic matter content degrade differently (ammoniacal nitrogen, nitrates, nitrites) in different parts of the distribution network. Using pre-chlorination, dictated by the organic load of the water source, has created the prerequisites for obtaining a drinking water with the statistically significant reduction of the indicator parameters levels, but favoring the occurence of disinfection by-products which may affect the health of consumers. The total THM had values below the maximum allowable concentration, chloroform being the predominant identified component. The presence of the other THM species was detected at much lower concentrations. Statistical data processing showed that the presence of THM precursors correlated with THM levels but not sufficient for their generation, even if in general they can be the basis for a valid prediction.

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