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VOLATILE ORGANIC DISINFECTION BY PRODUCTS DETERMINATION IN DISTRIBUTION SYSTEM FROM CLUJ NAPOCA

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ABSTRACT. Chlorine is one of the most used water disinfectant agent used on the world. The use of chlorine in the treatment of drinking water has virtually eliminated waterborne diseases, because chlorine can kill or inactivate most microorganisms commonly found in water. The majority of drinking water treatment plants in Romania use some form of chlorine to disinfect drinking water: to treat the water directly in the treatment plant and/or to maintain a chlorine residual in the distribution system to prevent bacterial regrowth. Unfortunately it's used results in formation of some disinfection by products (DBPs) that are suspected from harmful effects on humans. Such of disinfection byproducts are trihalomethanes (THMs). Trihalomethanes are a group of volatile organic compounds that can form when the chlorine used to disinfect drinking water reacts with naturally occurring organic matter (e.g., decaying leaves and vegetation). The preliminary results presented in this paper shown that the THMs levels from Gilau Water treatment Plants and Cluj-Napoca distribution system. The results have higher values in the summer period relative to other seasons.

***Keywords*:** *Volatile disinfection by-products, Trihalomethanes, Chlorine, Water Treatment Plant.*

INTRODUCTION

Chlorine is one of the most common disinfectant agents used in Water Treatment Plant (WTP) from Romania. The drinking water disinfection process with chlorine has been carried out since the dawn of the 20th century to eradicate and inactivate the pathogens from water. In addition to inactivating pathogens in the source water, chlorine are also used as oxidants in drinking water treatment to: remove taste and odors, oxidize iron and manganese,

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maintain a residual to prevent biological regrowth in the distribution system, improve coagulation and filtration efficiency and prevent algal growth in sedimentation basins and filters [1]. Chlorine's popularity is not only due to lower cost, but also to its higher oxidizing potential, which provides a minimum level of chlorine residual throughout the distribution system and protects against microbial recontamination [2, 3]. However, in 1974, it was discovered that the chlorination of water resulted in the production of trihalomethanes (THMs) due to reaction of chlorine with natural organic matter (NOM) present in all type of water, referred as precursor of THMs formation [4,5]. Since 1980' THMs have raised significant concern due to evidence of their adverse human health effects, in special cancer and reproductive disorders [6,7].

Because of this unwanted effects of chlorination process USEPA in November 29, 1978, has promulgated the first legislation (interim total THMs standard) to limit the concentration of total THMs (TTHMs) in drinking water.

In Romania the regulation and monitoring of THM has became a current issue in connection with Romania's entry to the UE and the fulfillment of the required drinking water standards. In order to minimize cancer risk, the Romanian has adopted the maximal permissible value fixed in the EU drinking water directive has been adopted by the Romanian legislation in 2002, granting the water companies a transition time of 10 years to meet the requested standards and accepting in the first 5 years a TTHM value of 150 μg/l. In terms of monitoring, the Romanian water law stipulates a minimal number of samples per year depending on the magnitude of the treatment plant. The local health authority carries out the monitoring.

Hence engineers are required to minimize the concentration of THMs in water in the distribution system.

Chlorine reacts with a wide variety of organics in water to give rise to haloform reaction and produce THMs. THMs are organohalogen compounds and they are named as derivates of the compound methane. THMs are formed when three of the four hydrogen atoms attached to the carbon atom in the methane compounds are replaced with atoms of chlorine, bromine and/or iodine [8]. THMs include chloroform – $CHCl_3$, dichlorobromomethane – $CHCl_2Br$, dibromochloromethane – $CHClBr_2$ and bromoform – $CHBr_3$. This complex reaction mechanism of THMs is controlled by parameters such as: concentration and type of precursors, concentration of chlorine, temperature, pH and time. The THMs formation process may be described by the following equation:

$$\text{NOM (Precursors)} + HOCl \rightarrow \text{Chlorinated organic intermediates} + HOCl \rightarrow CHCl_3 \quad (1)$$

$$\text{Natural bromide in water } (Br^-) + HOCl \rightarrow Br_2 + Cl^- \rightarrow CHCl_2Br/CHClBr_2/CHBr_3 \quad (2)$$

RESULTS AND DISCUSSIONS

THM measurements in Gilau WTP from Cluj: During the THMs analysis the main founded THMs species detected in the water sample was the $CHCl_3$. The $CHCl_3$ concentration differed from month to month during the years. Usually higher $CHCl_3$ concentration was found in the wormer season, than in the winter season. In Gilau WTP and distribution system the highest $CHCl_3$ concentration was detected in August 2007 – 81.1 μg/L. The measurement shows that the $CHCl_3$ concentration increased in the distribution system. The chloroform concentration range in the WTP at the exit of reservoir sampling point was in the range 8 μg/L (March 2007) and18.75 μg/L (November 2007). That could be explain by the fact in the winter season in the water are present lower concentration of NOM than in summer season due to low temperature and light. From that reason less chlorine concentration are required for water disinfection process. During the measurements was observed also that the chloroform concentration increased with distance. Started from the Exit of the reservoir from the WTP (considered 0 point) the chloroform concentration increased with 30 % at the enter of the city (located at 18 km from the Gilau WTP) and in the city center (located at 25 – 30 km from the Gilau WTP) the chloroform concentration was double or almost much with three times. That shows the THMs concentration increased with distance – see table 1.

Table 1. *$CHCl_3$ concentration measured in 2006 – 2008 at the Gilau WTP and Cluj.*
*Obs: Ex.R. – represent exit of reservoir, En.C. – enter of city, Cen. – center of city.

$CHCl_3$ concentration (μg/L)			
	2007		
Month	Ex.R.	En.C.	Cen.
January	25.4	31.1	40.4
February	12.0	31.6	48.6
March	8.0	18.7	21.6
April	8.2	29.2	33.8
May	14.7	40.6	50.2
June	19.2	60.2	66.3
July	21.0	65.2	69.0
August	28.0	69.0	81.1
September	24.5	39.58	52.4
October	20.1	32.8	47.9
November	18.75	24.9	35.9
December	9.32	12.78	21.7

Factors affecting THM formation: Manny research showed that are several factors affecting the formation potential of THMs. Previous research studies have shown that the major variables that affect THM formation are: chlorine dose and residual, concentration and nature of NOM (mainly humic substances), contact time, pH, temperature of water, and the presence of inorganic ions like bromide [9-13]. In general, higher THM concentrations are expected at higher levels of the above mentioned parameters [2].

Increase of chlorine dose has been reported to have positive influence of DBPs yield. The same is true for increased concentrations of natural organic matter and increased temperature. The presence of bromide ion shifts the speciation of DBPs to more brominated analogues, while increased pH can enhance the formation of some categories of DBPs, e.g. THM, and inhibit the formation of some others, e.g. haloacetonitriles and haloketones [10-11].

The type of raw water also affects the THM levels. Generally, ground waters are naturally protected from runoff NOM, while the difference in occurrence of DBP precursors in river and lakes depends on geological, physical and environmental factors (trophic stage, watershed soil characteristics and land use, lake size, river flow rate, etc.) [2].

Chlorine dose: During the studies it was observed that one of the main important factor that affect the THMs formation in the distribution system in the four WTP studied was the chlorine dose that was applied in the WTP in water disinfection purposes.

In Gilau Water Treatment Plant was added different chlorine dose during the year, the chlorine dose could differed day-by-day as the water matrix was changed due to seasons, temperature, pH and the NOM concentration presented in the raw water. So in Gilau WTP the company has set 2 different chlorine dose range, as function of season: for summer season the chlorine dose range that was added to water for disinfection was set between 0.7 – 0.9 mg/ L and for winter season the chlorine dose set was in the range of 0.5 – 0.7 mg/L. After several measurement has shown that in the period when higher chlorine dose was used the $CHCl_3$ concentration increased – as shown in figure 1.

Nature and Concentration of NOM: Properties of NOM play an important role, since activated aromatic content of NOM increases THM formation [12, 13]. Singer (1999) in his researches shows that the THMs formation is relatively higher for the humic acid fraction, presumably because of the greater aromatic carbon content of the fraction [14]. Manny researcher works showed a linear relationship between chlorine consumption and the activated aromatic carbon content of the various humic and fulvic acid. In addition, NOM contains hydrophobic and hydrophilic materials, the nature and distribution of which may vary with different types of vegetation in the watershed and different species of algae in water. This results in varying influence of NOM on DBP formation [15].

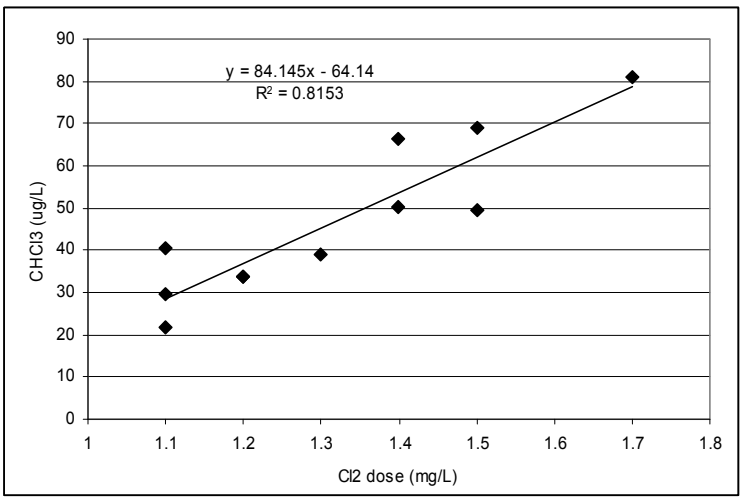

Figure 1. *Chlorine dose as function of $CHCl_3$ concentration in Gilau WTP*

In the WTP the presence of the natural organic matter was determinate with consumption of $KMnO_4$ mg/L – CCO Mn [mgKMnO4/L] – colorimetric method. The presence of the organic matter in the raw water is determinate once at the middle of day in every day in Gilau WTP. The results obtained showed that in the period when the NOM presence in water was higher also the $CHCl_3$ increases – see figure 2.

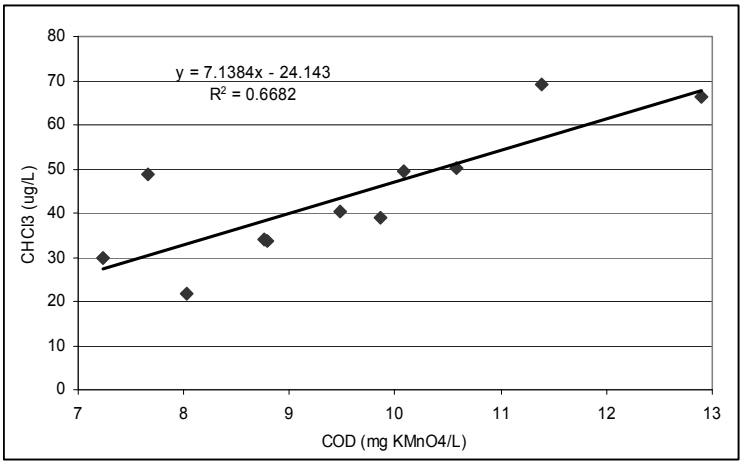

Figure 2. *Relationship between $CHCl_3$ (μg/L) and presence of natural organic mater in water*

Temperature/Season: When temperature increases, reactions are faster and a higher chlorine dose is required, leading to higher formation of THMs. Subsequently, THMs concentrations are expected to be higher in summer than in winter [11; 17; 18-21].

After THMs analysis in every month, the results show that in the winter season the THMs concentration were much lower that in the summer season, with almost 50 %. That could be explain by the fact that in some cases where the ice cover protects surface raw waters, the THM concentrations are lower due to lower water temperature and NOM. In these conditions, the chlorine demand is lower, therefore, the chlorine dose required to maintain adequate residual in the distribution system is also less.

In Gilau WTPs which used as disinfectant agent the chlorine the mean of total trihalomethanes (TTHM) levels for summer, fall, winter, and spring was: 72.17 µg/L, 40.716 µg/L, 30.606 µg/L and 35.23 µg/L respectively;

This study showed that the highest TTHM concentrations were found in the summer and fall seasons, and the lowest TTHM concentrations were present in the winter and spring. Since higher doses of chlorine were used in the warm summer and fall months to ensure prevention of microbiological problems, it was to be expected that this, in combination with warmer water temperatures, would lead to higher TTHMs concentration during the summer and fall seasons.

pH: Several studies have been made to investigate the effect of pH on THMs concentrations. The studies have shown that THM concentrations increases with increasing pH – as shown in figure 3, that could be explain by the fact that THMs formation is mainly attributed to the reactions of the chlorinated intermediates with hydroxide ion in the presence of a small amount of free chlorine.

Bromide: Recent studies have examined the relationship between bromide concentration in a drinking water supply and THMs formation. Based on the differences in bromide concentration, it is inferred that substantial variations in THM formation (and THM species) can be expected. Studies have shown that as the concentration of bromide increases, the concentration of TTHMs increases and more brominated THMs forms because there is more bromide present in the water source for the organics to react with. In the presence of bromide ion (Br-), more brominated and mixed chloro-bromo derivatives are formed [22-25]. When bromide is present, chlorine in the form of hypochlorous acid-hypochlorite ion (HOCl-OCl-) oxidizes bromide ion to hypobromous acid-hypobromite ion (HOBr-OBr-). A mixture of HOCl and HOBr can lead to the formation of both chlorinated and brominated by-products [26].

During the analysis of the THMs species in WTPs the brominated THMs species were very lower all the time, the total brominated THMs species never exceed 10 µg/L. So in the Gilau WTP the only brominated THMs species

that was found was $CHCl_2Br$ and its highest concentration was 9.69 µg/L. After that results we could concluded that in all WTPs the bromide concentration are almost inexistent or in very less concentration.

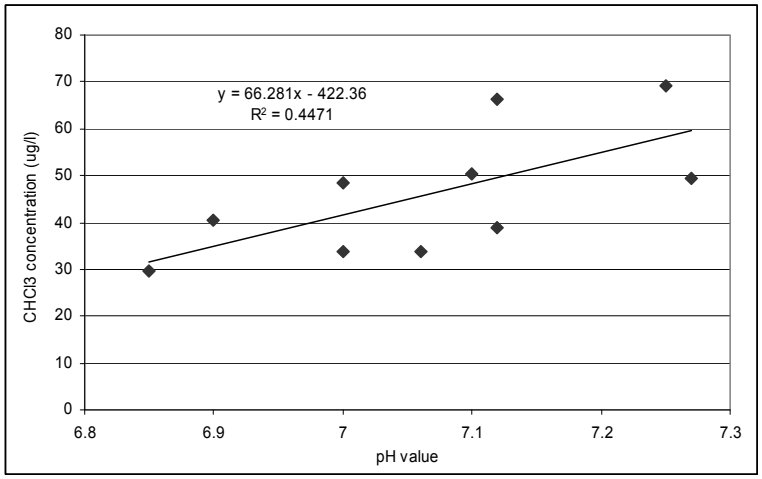

Figure 3. *Relationship between $CHCl_3$ ($\mu g/L$) and pH value of water.*

CONCLUSIONS

This study examined the trihalomethanes formation and they concentration in different sampling point take from different sampling points in Cluj-Napoca. Following conclusions were drawn based on the results of the measurements conducted with water samples of every month in 2007.

Chloroform was the determinate trihalomethanes species observed after the chlorination of reservoir water in all of the sampled months. Brominated compounds of trihalomethanes wasn't observed, just $CHCl_2Br$ but in very slow concentration. We can suppose for that reason, the bromine compounds in the raw water is very slow or almost inexistent.

The major factor that influences the trihalomethanes formation is the temperature that is clearly praise in chloroform concentration measured in different months of year. In the months like July, August, September and October when the temperature was highest (21 – 24 °C water temperature) also the chloroform concentration was high (66.3 – 81.1 µg/L) and when the water temperature wasn't high (2.8 – 3.7 °C) the chloroform concentration was between 21.7 – 40.4 µg/L. The major differences in temperature and pH value affect trihalomethanes potential formation (THMFP), with more volatile THM species being produced at the higher temperature and pH. Also we can concluded the season when the water matrix is change from the winter season to summer season also have a seriously influence on trihalomethanes formation.

MATERIALS AND METHODS

Sampling: Several samples were collected from different sampling point of the Gilau Water Treatment Plant (WTP) and distribution system from Cluj-Napoca – located in Cluj jurisdiction. Gilau WTP has as water sourced the Somesul Mic river basin and also Tarnita Storage Lake. All the samples were collected in every month of 2007. The sampling contains the following samples:

Gilau WTP:

- raw water, filtrated water, chlorinated water, exit reservoir – sampling points that are located in the WTP;
- Sapca Verde, Beer Factory, Chemistry Faculty, Environmental Faculty and Public Health Institute – sampling points that are located in the distribution system.

All water samples were collected and stored in 40 L vials and closed with Teflon lined screw cap and they were preserved with sodium thiosulfate ($Na_2S_2O_3$) at 4^0C until the analysis. All samples were measured between in 1 and 7 days after sampling.

THMs analysis: THMs were carried out by Thermo Finningan U.S.S. Trace GC Ultra gas chromatography with electron capture detector (GC-ECD) with TriPlus HS auto sampler. The analysis was made using headspace technique. 10 ml of sample was filled into 20 ml headspace vials and closed with Teflon lined screw cap. After that the samples were equilibrated in an oven at 60 °C for 45 minutes, 1 ml of the headspace was then injected into the GC (Cyanopropylphenyl Polysiloxane column, 30 m x 53 μm, 3 μm film thickness, Thermo Finnigan, USA). The column program was 35 °C (hold time 3 minutes), 15 °C/minutes to 200 °C (hold time 3 minutes). The inlet was set at 200 °C.

The standard stock solution containing 2000 μg/l of each Trihalomethanes from Restek (Bellefont, U.S.) was used. THM working standard solutions (100 mg/l, 4mg/l) were prepared through dilution of the stock solution in 10 ml Methanol. The calibration standards were made using that THM stock solution and the calibration were prepared for the range 0 – 100 μg/L in mineral water Izvorul Alb.

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