

FACTORS AFFECTING THM FORMATION IN THE DISTRIBUTION SYSTEM OF CLUJ, ROMANIA

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Abstract. Trihalomethanes (THMs) are formed from the reaction of natural organic matter (NOM) present in all types of water, with chlorine used as a disinfectant in water treatment. THMs formed in the Cluj-Napoca distribution system were studied between July 2006 and March 2008 with gas chromatography with an electron capture detector (GC-ECD) using the headspace technique (HS). To identify factors that influence the THM formation, the chlorine decay and THM formation kinetics were followed in laboratory experiments every month during the study. Total chlorine, free chlorine and monochloramine were analyzed using a spectrophotometric method. Several factors affecting the formation of THMs were identified. The main factors having a high influence on THM formation in the distribution system from Cluj-Napoca were the chlorine dose, presence of the natural organic matter (NOM) in water, reaction time, temperature/season and the pH. The main THM identified was chloroform with a maximum concentration of 72 µg/L. Because of the low bromide concentration of the source water (5-7 µg/L), brominated THMs were always below 10 µg/L. Therefore the Romanian drinking water standard for total THM was never exceeded.

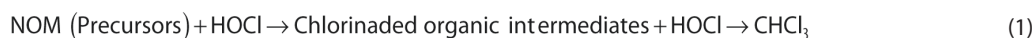
Key words: disinfection by-products, THM, GC-ECD, chlorine consumption, kinetic model.

INTRODUCTION

The Gilău water treatment plant (WTP) provides drinking water for the approximately 600000 inhabitants of Cluj-Napoca, Gherla and several smaller villages downstream as Apahida, Aghireş, Cojocna, Jucu, etc. Its principal water sources are the storage lakes Gilău and the Someşul Cald River. In the Gilău WTP the disinfection process is based on the addition of chlorine gas. The chlorine gas is added manually to achieve a free chlorine residual at the exit of reservoir between 0.5 –

0.7 mg/L Cl₂ in the winter season and 0.7 – 0.9 mg/L Cl₂ in the summer season (Truţă L., 2005). THMs are disinfection by-product classes that are formed after chlorine addition, due to the reaction of chlorine with natural organic matter (NOM). Its formation is related to the chlorine dose and contact time and the chemical properties of the particular water matrix (A. H. Duong *et al.*, 2003).

The THM formation process may be described by the following equations:



THMs have raised significant concern due to evidence of their potential adverse human health effects, such as cancer and possibly reproductive disorders (Cantor *et al.*, 1988; Graves *et al.*, 2002). Because of their possible adverse health effects, in Romania the regulation and monitoring of THM has become a current issue in connection with Romania's entry to the European Union (EU) and the fulfillment of the corresponding required drinking water standards set in the EU

drinking water directive (Directive 98/83/EC, 1998). These values have 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 total THM (TTHM) value of 150 µg/l. As for monitoring, the Romanian water law stipulates a minimal number of samples per year depending on the size of the treatment plant (L. 458/2002; L. 363/2004; H.G. 669/2004).

To assess information about the parameters that have an influence on THM formation in the distribution system, laboratory chlorination experiments with filtrated water collected after one of the sand filters from the Gilău WTP were carried out every month in the period from July 2006 to March 2008. The parameters with potential influence on the THM formation were investigated. Also the THM concentrations obtained in laboratory experiments were compared with values measured in the distribution system to assess the possibility to simulate the THM formation process.

MATERIALS AND METHODS

ANALYTICAL METHODS

For THMs analyses from the WTP Gilău and distribution system several samples were collected as described in the following: raw water, filtrated water, chlorinated water, exit reservoir – sampling points that are located in the WTP. In addition, samples were taken in the distribution system at the entrance of the city (Șapca Verde, Beer Factory), center of the

city (Chemistry Faculty, Environmental Faculty) and almost at the exit of the city (Public Health Institute).

THM analysis was carried out by Thermo Finnigan U.S. Trace GC Ultra gas chromatography with electron capture detector (GC-ECD) and TriPlus HS auto sampler. The analysis was made using the headspace technique. 10 mL of sample was filled into 20 mL headspace vials and closed with a 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 injected into the GC (cyanopropylphenyl polysiloxane column, 30 m x 53 mm, 3 μm film thickness, Thermo Finnigan, USA). The TriPlus HS auto sampler and GC-ECD working parameters are given in Table 1. The standard stock solution used for THM analyses contained 2000 μg/mL of each trihalomethanes (Restek, Bellefont, USA). 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 calibration curves were prepared in the range 0 – 100 μg/L in the mineral water Izvorul Alb (village Dorna Căndrenilor, Romania).

Table 1 GC-ECD and TriPlus HS auto sampler operation conditions

GC - ECD	TriPlus HS
Carrier gas flow: nitrogen (N ₂) 30 mL min ⁻¹	Incubation time: 45 min
Make up: nitrogen (N ₂) 30 mL min ⁻¹	Incubation mode: constant
Split ratio: 1:5	Agitator temperature: 60°C
Injector temperature: 200°C	Agitator on: – 20 sec/ Agitator off: – 20 sec
Detector temperature: 300°C	Syringe temperature: 80°C
Oven temperature: 35°C (hold time 3 minutes), 15°C/minutes to 200°C (hold time 3 minutes)	Injection depth: 35 mm
	Injection speed: 40 mL/min
	Filling volume: 1.2 mL
	Filling counts: 1 / Filling delay: 0 sec
	Post injection syringe flush: 30 sec

The chlorine concentration was determined with the ABTS (2,2-azino-bis(3-ethyl-benzo-thiazoline)-6-sulfonic acid diamonium salt) colorimetric method at 405 nm and ABTS was purchased from Fluka (Buchs, Switzerland) (Pinkernell *et al.*, 2000) It was also checked with the DPD method (N,N-Diethyl-1,4-phenylendiammoniumsulfat) that was purchased from Merck (Darmstadt, Germany). The standard DPD method 8167 (powder pillow) was used at 530 nm wavelength and measurements were made with a Dr Hach 2800 spectrophotometer. With the DPD method, the concentration of NH₂Cl was determined by subtracting the free chlorine concentration from total chlorine and in the ABTS method the free chlorine concentration was determined by subtracting the NH₂Cl concentration from the total chlorine concentration. The standard deviation between the two colorimetric methods for total chlorine, free chlorine and monochloramine were in the range: 6.1 – 9.1 %.

KINETIC EXPERIMENTS

For kinetic experiments, pretreated water was collected at the Gilău WTP after sandfiltration once per month and stored in 5 L plastic bottles at 4°C without adding any preservatives until the chlorination experiments were performed. For the kinetic experiments, 500 ml of filtrated water was filled into a Schott bottle and the pH was adjusted to the desired value by addition of NaOH (0.5 M) or H₂SO₄ (0.1 M) from "Reactivul" București (București, Romania) and from Merck (Darmstadt, Germany), respectively.

In order to determine factors that affect THM formation, the chlorine decay and THM kinetics were performed under two conditions: *baseline condition* (2.5 mg/L Cl₂, pH 7 and 21°C) and *seasonally variable condition* (where the pH, water temperature and chlorine dose were maintained the same as during sampling at the WTP). For experiments un-

der baseline conditions, the water was buffered with 12.5 ml of a $\text{Na}_2\text{B}_4\text{O}_7$ solution (0.5 M, purchased from "Reactivul" București – București, Romania) to keep the pH at 7. A diluted chlorine solution (from 95 % purity of Cl_2 solution, Sun Industries, Ilfov, Romania) for a desired chlorine dose was prepared. The respective chlorine dose was added to the filtrated water and stirred for 40 s. For each desired reaction time, two 8 mL water samples were taken with a dispenser and total chlorine, free chlorine and monochloramine concentrations were measured colorimetrically according to the methods described above.

RESULTS AND DISCUSSION

In the water samples collected from the Gilău WTP and distribution system from Cluj-Napoca, chloroform (CHCl_3) was the most commonly found THM in drinking water and also at the highest concentration from the four THMs species. However, its concentration never exceeded the EU drinking water standard of 100 $\mu\text{g/L}$.

Chlorine dose: During the THM analyses and laboratory kinetic experiments it was observed that the main parameter that influences the THM formation was the chlorine dose. In the Gilău WTP different chlorine doses were added during the year. The chlorine doses could also vary from day to day as the raw water matrix was changed due to seasons (e.g., temperature, pH and the NOM concentration). In the Gilău WTP, two different chlorine dose ranges are set, as shown above, to adapt to seasonal changes. As shown in Fig. 1, higher chlorine doses typically result in higher CHCl_3 concentrations.

Also, in the laboratory kinetic experiments, an increase of the CHCl_3 concentration was found with increasing chlorine doses. For example, with a chlorine dose of 0.8 mg/L, the CHCl_3 concentration formed after 8 – 10 hours was in the range of 17.8 – 18.6 $\mu\text{g/L}$ and with a higher chlorine dose (2.5 mg/L), the CHCl_3 concentration increased to 28.0 – 31.0 $\mu\text{g/L}$.

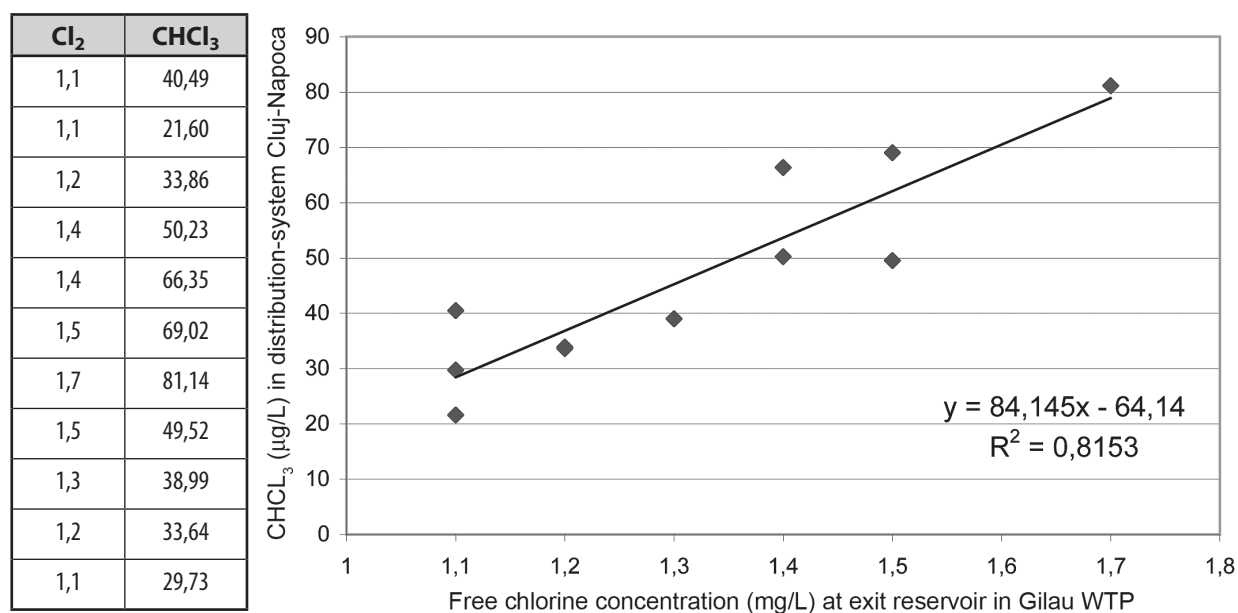


Fig. 1 CHCl_3 concentration in the distribution system of Cluj-Napoca as a function of the chlorine dose added at the Gilău WTP

This could also be observed in laboratory kinetic experiments (Figs. 2, 3) where higher chloroform concentrations were measured when higher chlorine doses were added to the water. The high level of chloroform may also be explained by the changes of the water matrix (as pH, temperature and NOM concentration) in different months of the year.

Natural Organic Matter (NOM): NOM includes humic substances, microbial exudates and other organic materials dissolved originating from soil and terrestrial vegetation or from biological processes in the water. They are present in all types of water in different amounts (Croue, *et al.*, 1999). NOM reacts with chlorine during disinfection processes and leads to the formation of THMs (Duong *et al.*, 2003). The COD concentra-

tion in the raw water was determined every day during the sampling campaign. The results obtained showed that there is a certain correlation between the NOM concentration and the CHCl_3 level after chlorination (see Fig. 4). During the study, the NOM concentration was always 30 – 50 % higher in the warmer season than in the cold season.

Reaction time: In Fig. 5 the CHCl_3 concentration measured in the WTP Gilău and the distribution system is shown for the entire sampling campaign. It can be seen that, increasing the time and also the distance from the Gilău WTP, the CHCl_3 concentration increased. This is in agreement to the data shown in Fig. 3 for laboratory studies.

MONTH	FEBRUARY 1 mg/L	APRIL 1.2	MAY 1.4	JULY 1.5	AUGUST 1.7
time (min)	free chlorine (mg/l)	free chlorine (mg/l)	free chlorine (mg/l)	free chlorine (mg/l)	free chlorine (mg/l)
0,333	0,989	1,188	1,391	1,512	1,717
0,666	0,946	1,096	1,326	1,392	1,659
1,00	0,916	1,032	1,132	1,250	1,521
3,00	0,883	0,907	1,067	1,175	1,425
6,00	0,826	0,873	1,012	1,116	1,352
12,00	0,784	0,794	0,978	1,061	1,285
20,00	0,681	0,714	0,874	0,988	1,212
30,00	0,653	0,693	0,823	0,878	1,110
40,00	0,635	0,661	0,794	0,806	0,994
50,00	0,593	0,606	0,745	0,735	0,962
60,00	0,505	0,568	0,713	0,698	0,922
120,00	0,410	0,451	0,649	0,599	0,807
180,00	0,357	0,406	0,583	0,521	0,741
240,00	0,321	0,380	0,545	0,481	0,669
300,00	0,316	0,357	0,491	0,450	0,602
360,00	0,298	0,334	0,455	0,408	0,552
420,00	0,284	0,307	0,418	0,372	0,498
480,00	0,265	0,282	0,410	0,338	0,487
540,00	0,252	0,271	0,397	0,316	0,448
600,00	0,229	0,264	0,397	0,315	0,421
630,00	0,230	0,259	0,394	0,307	0,401

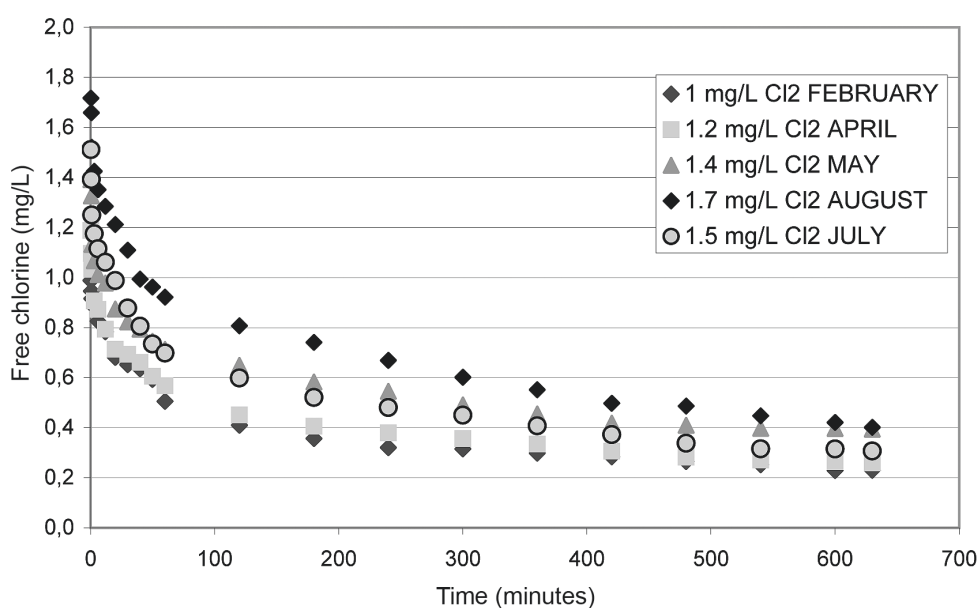


Fig. 2 Different chlorine dose consumption in water matrix in different months of the analysis

Time	2.5 mg/L	1.6 mg/L	2.0 mg/L
0	u.l.d.	0,15	u.l.d.
5	7,04	7,06	7,01
10	17,02	20,90	19,33
20	25,62	29,03	23,42
40	29,32	36,01	26,12
60	34,02	40,52	29,75
120	44,51	46,92	40,11
180	53,62	51,03	52,00
240	61,03	55,93	58,99
300	67,89	59,64	62,18
360	74,62	62,33	66,72
420	78,03	64,90	68,93
480	81,89	67,13	72,56
540	84,51	69,89	75,11
600	85,32	70,97	78,00
630	86,10	71,54	79,23

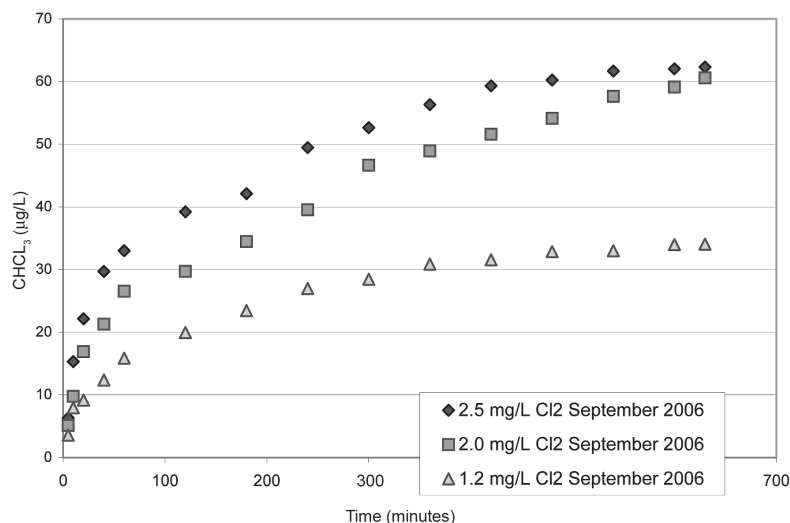


Fig. 3 CHCl₃ (µg/L) rate formation when different chlorine doses were added to the same water matrix (September 2006)

COD (mg KMnO ₄ /L)	CHCl ₃ (µg/L)
7,28	30,12
7,86	48,99
8,01	21,45
8,89	34,68
9,48	40,49
9,97	39,47
10,24	50,27
10,68	51,09
11,67	69,87
12,84	67,34

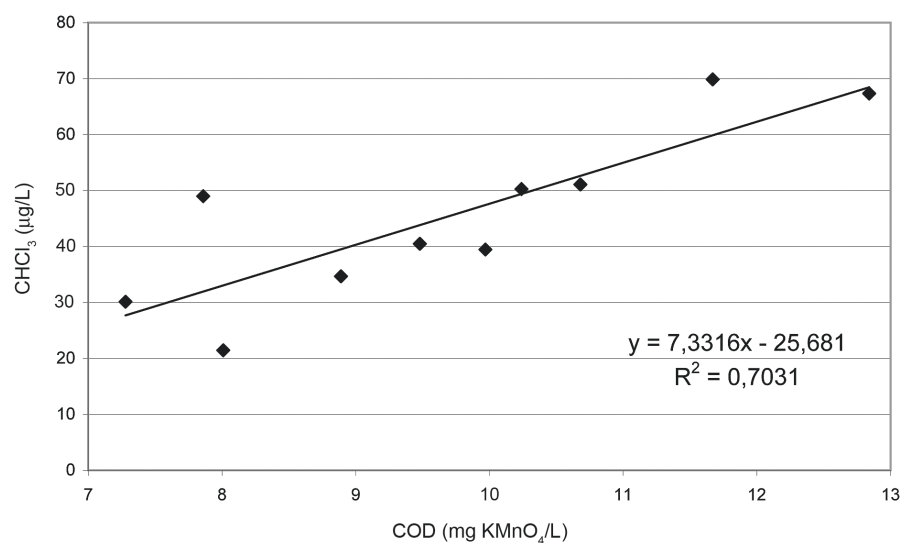


Fig. 4 Relationship between CHCl₃ (µg/L) and presence of natural organic mater in water

The experiment was conducted at the Gilău WTP to investigate the THM formation after different contact times. Over 4 samples were collected in eight groups, each group representing an increasing residence time from the point of disinfection. The average concentration of TTHMs at the eight point in and after the WTP were 5.0 µg/L, 11.0 µg/L, 16.1 µg/L, 25.4 µg/L, 32.4 µg/L, 36.5 µg/L, 38.8 µg/L and 39.4 µg/L, respectively. In kinetic laboratory experiments conducted with natural water during this investigation of the kinetics of the formation of THMs and of chlorine consumption it was ob-

served that, as the reaction time increased, the formation of CHCl₃ also increased.

Temperature/Seasons: The THM analyses in Fig. 5 show, that during winter, the CHCl₃ concentrations were much lower than during the summer season, with a difference of almost 50 %. That could be explained by the fact that the THM formation is slower due to lower water temperatures (in winter season the temperature of water is between 2.7 – 6.3°C) and lower NOM concentrations (from December – February, COD were in the range of 6.9 – 7.6 mg/L). Under these condi-

	2006						2007						2008								
	July	Aug	Sept	Oct	Nov	Dec	Jan	Feb	March	April	May	June	July	Aug	Sept	Oct	Nov	Dec	Jan	Feb	March
1 Raw water	0,6	0	0	0	1,02	0	0	0	0	0	0	0	0	0	0	0	0,52	0	0	0	
2 Filtrate water	4,9	0	0	0	0	0	0	0	0	0	0	0	0	0	2	0	0	0	0	0	0
3 Exit Reservoir	12,4	14,28	8,4	30,3	4,01	2,22	25,44	12,08	8,09	8,22	14,75	19,26	31,05	28,02	31,0	18,5	11,5	4,9	7,6	6,5	10,1
4 Sapca Verde	18,7	46,83	47,7	51,6	13,43	9,34	27,06	28,36	16,71	20,81	36,11	58,44	63,08	64,31	54,2	22,3	14,2	5,6	8,2	9,5	19,6
5 Beer Factory	28,4	55,08	47,0	55,8	7,98	6,36	32,15	31,62	18,70	29,26	40,69	60,28	65,24	69	59,3	28,5	14,1	11,2	14,4	14,3	25,4
6 Chemistry Faculty	35,2	66,8	66,9	72,8	13,58	27,77	38,51	48,6	18,99	27,12	43,05	65,31	67,29	78	65,1	29,6	16,5	17,6	16,9	21,9	34,9
7 Environmental Science Faculty	37,1	60,3	66,6	65,8	27,26	21,08	35,9	36,73	20,90	32,41	54,00	64,28	71,33	76,25	68,4	33,5	19,2	19,4	19,0	24,6	44,2
8 Institute of Public Health	23,2	68,4	71,1	41,4	16,54	28,17	40,49	48,6	21,60	33,86	50,23	66,35	69,02	81,14	67,8	37,2	27,5	18,6	18,6	29,3	47,6

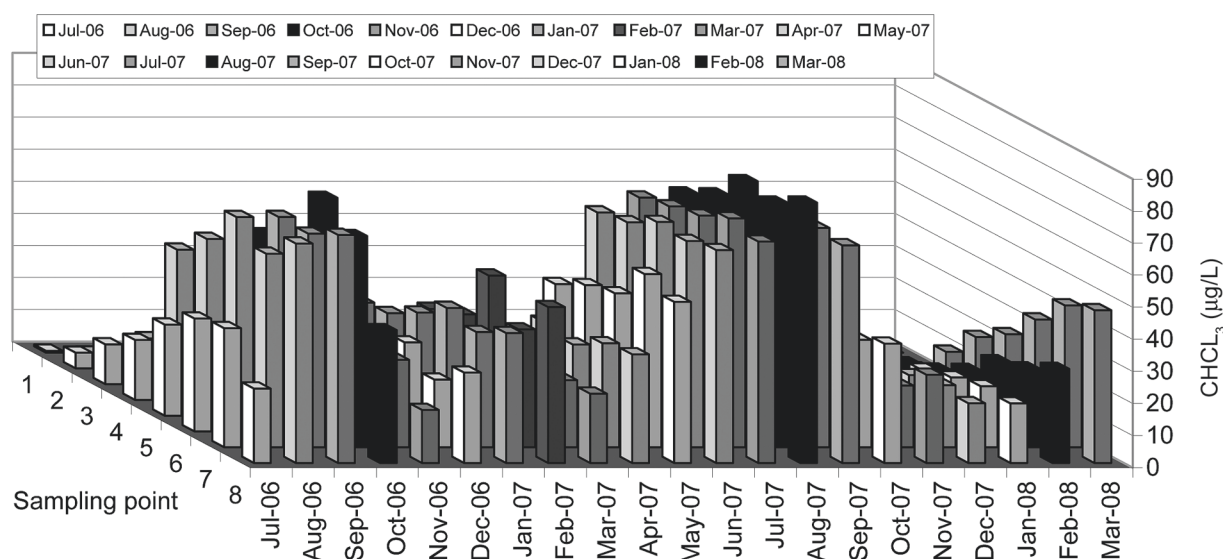


Fig. 5 CHCl_3 ($\mu\text{g/L}$) in different months during the study in all the sampling points from Gilău WTP and Cluj-Napoca distribution system. 1 – raw water/ 0 km; 2 – filtrate water/ 1 km; 3 – exit reservoir/ 5 km; 4 – Şapca Verde/ 18 km; 5 – Beer Factory/ 20 km; 6 – Chemistry Faculty/ 22 km; 7 – Environmental Faculty/ 26 km; 8 – Institute of Public Health/ 31 km

tions, the chlorine demand is lower, therefore, the chlorine dose required to maintain an adequate residual in the distribution system is also smaller. The mean THM levels in the Gilău WTP for summer, fall, winter, and spring were: 72.1 $\mu\text{g/L}$, 40.7 $\mu\text{g/L}$, 30.6 $\mu\text{g/L}$ and 35.2 $\mu\text{g/L}$, respectively.

pH: Several studies have been made to investigate the effect of pH on THM concentrations. The studies, conducted with natural water collected from the Gilău WTP, have shown that the pH has an influence on THM concentrations. An increase of 10 – 25 % was measured for a change of pH between 6.5 and 7.9.

Bromide: Many studies have examined the relationship between bromide concentration in a drinking water supply and THM 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 form (Krasner *et al.*, 1993; Heller-Grossman *et al.*, 1993; Pourmoghaddas and Stevens, 1995). When bromide is present, chlorine, in the form of hypochlorous acid (HOCl) oxidizes bromide ion to hypobromous acid (HOBr). A mixture of HOCl and HOBr can lead to the formation of both chlorinated, brominated and mixed by-products (Pourmoghaddas and Stevens, 1995).

During the analysis of the THM species in the Gilău WTP, the brominated THMs were very low. The total brominated trihalomethanes species never exceeded 10 $\mu\text{g/L}$. In the Gilău WTP the only brominated THM that was found was CHCl_2Br and its highest concentration was 9.7 $\mu\text{g/L}$ in August 2007. This can be explained by the low levels of bromide (the range of the bromide concentration during the sampling campaign was 5 – 7 $\mu\text{g/L}$) in the source water.

CONCLUSIONS

The main THM formed during water treatment and in the distribution system of Cluj is chloroform, but its concentration never exceeded the maximum contaminant level of 100 µg/L that was set by the Romanian legislation. Since the bromide levels in the source waters are very low (5 - 7 µg/L) mixed THM, such as CHCl₂Br, CHClBr₂ and CHBr₃ were only detected

in low concentrations (< 10 µg/L). Several factors affecting the formation of THMs were identified: The most important factors were the chlorine dose, the presence of the natural organic matter (NOM) in water, reaction time, temperature/seasons and pH. Therefore, the CHCl₃ concentrations in the Cluj-Napoca distribution system were found to be highest in summer (≤ 80 µg/L) and lowest in winter (≤ 30 µg/L)

REFERENCES

- TRUȚĂ, L., 2005. Apa Clujului, Editura Studia, Cluj-Napoca, ISBN 973-8390-15-X
- CANTOR, K. P., LYNCH, C. F., HILDESHEIM, M. E., DOSEMECI, M., LUBIN, J., ALAVANJA, M., CRAUN, G., 1988. Drinking water source and chlorination by-products I. Risk of bladder control. *Epidemiology*, 9 (1), 21–28
- CROUE, J. P., DEBROUX, J. F., AMY, G. L., AIKEN G. R., LEENHEER, J. A., 1999. Natural Organic Matter: Structural Characteristics and Reactive Properties, In: Formation and Control of Disinfection By-Products in Drinking Water, eds., P.C.Singer, pp. 65-93, American Water Works Association, USA
- DUONG, A. H., BERG, M., HOANG, M. H., PHAM, H. V., GALLARD, H., GIGER, W., GUNTEN U., 2003. Trihalomethane formation by chlorination of ammonium- and bromide-containing groundwater in water supplies of Hanoi, Vietnam. *Water Research*, 37, 3242–3252,
- GRAVES, C. G., MATANOSKI, G. M., TARDIFF, R. G., 2002. Weight of evidence for an association between adverse reproductive and developmental effects and exposures to disinfection by-products: a critical review. *Regul Toxicol Pharmacol*, 34, 103–124
- HELLER-GROSSMAN, L., MANKA, J., LIMONI-RELIS B., REBHUN, M., 1993. Formation and distribution of haloacetic acids, THM and TOX in chlorination of bromide-rich lake water, *Water Research*, 27, 1323-1331
- KRASNER, S. W., GLAZE, W. H., WEINBERG, H. S., DANIEL, P. A., NAJM, I. N., 1993. Formation and Control of Bromate During Ozonation of Waters Containing Bromide, *Journal of American Water Works Association*, 85, 1, 73- 81
- DIRECTIVE 98/83/EC, 1998. Official Journal of the European Community L 330, EU, 1998
- L. 458/2002, 2002. Parlamentul României, Lege privind calitatea apei potabile. Annex 1, table 3
- L. 363/2004, 2004. Parlamentul României 2004. Lege pentru modificarea și completarea Legii nr.458/2002. Annex 1, table 2
- H.G. 669/2004, 2004. Guvernul României, Hotărâre pentru aprobarea Normelor de supraveghere, inspecție sanitară și monitorizare a calității apei potabile. 669/26.VII.2004. Annex 1, table 1 – 2
- PINKERNELL, U., NOWACK, B., GALLARD, H., U VON GUNTEN, 2000. Methods for the photometric determination of reactive bromine and chlorine species with ABTS. *Water Resources*, 34: 4343-50
- POURMOGHADDAS, H., STEVENS, A. A., KINMAN, R. N., DRESSMAN, R. C., MOORE, L. A., IRELAND, J. C., 1993. Effect of Bromide Ion on Formation of HAAs During Chlorination, *Journal of American Water Works Association*, 85, 1, 82-87
- POURMOGHADDAS, H., STEVENS, A.A., 1995. Relationship between trihalomethanes and haloacetic acids with total organic halogen during chlorination, *Water Research*, 29, 2059-2062