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Water pollution

THE INCIDENCE OF BY-PRODUCTS (THMs) DISINFECTION IN DRINKING WATER

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Abstract. The paper presents some aspects related to the incidence of trihalomethanes (THMs) disinfection by-products, in drinking water obtained from various natural resources: surface water (rivers, barrier lakes) and ground water (bank infiltration water, deep ground water). In order to set up the quality of drinking water and its compliance with the enforced legislation, a number of 27 DWTPs was investigated. The Romanian water companies which are included in the analytical investigation program were: Timisoara, Deva, Drobeta – Turnu Severin, Botosani, Brasov, Turda, Satu Mare, Bistrita – Nasaud, Oradea, Galati, Cernavoda, Tulcea. According to the nature of raw water and the pollution context, the applied treatment technologies for water potabilisation are based on classical methods: chlorine disinfection or aeration/pre-chlorination – sand filtration – disinfection for ground water and pre-chlorination (optionally) – coagulation flocculation – settling – sand filtration – final disinfection for surface water. The performed analyses emphasised the compliance of THMs content with the imposed concentration by Law 458/2002 and Law 311/2004 (THMs = 100 μg/l) for almost all samples, with three exceptions: Saveni-Botosani (THMs = 121 μg/l), Santamarie Orlea-Deva (THMs = 545 μg/l), Oradea (THMs = 140.44 μg/l).

Keywords: drinking water, THMs.

AIMS AND BACKGROUND

In Romania, drinking water is produced from surface water (60%) and groundwater (40%).

Surface water, more exposed to anthropogenic pollution as groundwater contains, besides natural ‘pollutants’, other organic/biological/microbial loads.

A large number of DWTPs (natural resource – surface water) is using chlorine for disinfection in the treatment process, and also as a primary oxidant, prior coagulation-flocculation step. Chemical pre-oxidation is necessary for removal of algae, tastes and odours and oxidising iron and manganese. Also, for most groundwater supplies, chlorination is the only applied treatment.

According to literature data, only 1% of chlorine used for disinfection is transformed in halogenated by-products (TOX) with different volatility degree. It

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must be mentioned that trihalomethanes (THMs) represent near 30% of the total organohalogenated compounds generated by water chlorination[1]. The maximum admissible concentration (MAC) of total THMs, for various European countries ranges from 30 to 100 μg/l. The limit stipulated by the EU Drinking water Directive 98/83/EC and also by Romanian legislation (L458/2002, L311/2004) is 100 μg/l for total THMs parameter, which represents the sum of the individual compounds concentrations (chloroform, bromoform, dibromochloromethane and bromodichloromethane). The parameter value accepted for five to ten years after the entry into force of the Directive is 150 μg THMs/l. In Romania, the previous legislation for drinking water quality (STAS 1342/91) had stipulated also limit value for chloroform (THMs = 100 μg/l, $CHCl_3$ = 30 μg/l).

THMs ($CHCl_3$, $CHBr_3$, $CHCl_2Br$, $CHClBr_2$) are included into volatile organohalogenated class (TOXV), generated by direct action of chlorine/hypochlorite ions or bromine (*in situ* generated product by reaction between chlorine and bromide salts) upon organic matter from natural resources.

Among the main classes of organic compounds (THMs precursors) with high THMs 'production' are mentioned humic and fulvic acids (natural organic matter–NOM), phenolic compounds, including substituted phenols, metabolites of algae, anilines and derivatives[2,3].

The THMs produced by chlorination of algal mass and extracellular products (EPC) are equally significant like those generated by chlorination of humic matter (especially fulvic acids). Chlorination of certain algal cells causes taste and odour producing organic substances to be released due to cell lysis. The organic substances, apart from producing taste and odour, also play an important role in the formation of THM[4].

In accordance with theoretical studies the high reactivity of humic acids is due to the polyhydroxibenzene matrix units (*meta*- and *para*-dihydroxyaromatic compounds), 1 mg/l of humic acids is generating about 25 ± 4 μg/l chloroform.

The main reactions of chlorine with THMs precursors are partial/total oxidation, substitution and addition.

The factors with high influence upon TOX formation (quantities, reaction rates) are: organic load of natural water resources (nature, molecular weight, concentration), generally evaluated by TOC parameter, ratio between chlorine and organic matter (Cl_2/TOC), temperature, contact time, pH, bromide concentrations[5].

Generally, from total THMs, chloroform is the mainly by-product (72-93%) formed by chlorination, in the absence of bromide ions.

THMs, at short-term exposure level above MAC, have not been shown ill health effects, but at long-term exposure levels they may cause liver, kidney or central nervous system problems and also may cause an increased risk of cancer. Among the THMs compounds, dibromochlormethane was most closely associated with cancer risk, followed in order by bromoform, chloroform and dichlorobromomethane[6].

The present study refers to the incidence of disinfection by-products in drinking water, obtained by the treatment of surface and groundwater in 27 DWTPs from Romania. Also, the evolution of THMs along the treatment steps, when pre-chlorination is performed and along the route: storage tanks – distribution network – consumer is emphasised[7].

EXPERIMENTAL

In order to establish the compliance degree of drinking water quality with the enforced regulations, a number of 27 DWTPs were investigated via direct control. Two sampling campaigns were performed in spring and summer time, in locations situated in various Romanian counties. The analysis of THMs from momentary preserved water samples was performed by a GC-ECD detector (GC equipment: 6890 N type, producer AGILENT TECHNOLOGIES firm). Among the other analysed parameters directly connected with THM generation, must be mentioned organic matter (TOC), free/total chlorine, turbidity and bromide ions, using standard techniques/methods.

RESULTS AND DISCUSSION

According to the nature of raw water, the THM levels analysis is presented, as follows:

- Table 1, Figs 1 and 2 – incidence of THMs in drinking water obtained from surface water (river water, barrier lakes – 9 case studies), and the evolution of THMs along the treatment steps when pre-chlorination was used (2 case studies);
- Table 2, Fig. 3 – incidence of THMs in drinking water from DWTPs (4 case studies) which use the Danube river as raw water and the evolution of THMs on the treatment step when pre-chlorination was used (1 case study);
- Table 3 – incidence of THMs in potable water obtained from groundwater (including bank infiltration water);
- Table 4, Fig. 4 – evolution of THMs in drinking water on the route: storage tank inlet – distribution network inlet – consumer.

Almost all the momentary samples are emphasising the compliance of THMs concentrations with the MAC stipulated by the Romanian/European legislation, with three exceptions: Saveni-Botosani DWTP (raw water–barrier lake Negreni), Santamarie Orlea DWTP (raw water–barrier lake Hateg), Oradea DWTP (raw water – the Cris river–right bank infiltration water).

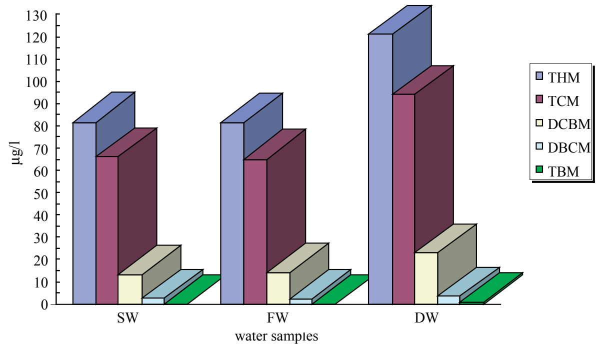

Fig. 1. THMs evolution of Saveni-Botosani DWTP steps (pre-chlorination-coagulation flocculation-setting–filtration–clorination/disinfection)
THM – trihalomethanes; TCM – trichloromethane; DCBM – dichlorobromomethane; DBCM – dibromochloromethane; TBM – tribromomethane; SW – settled water; FW – filtered water; DW – drinking water; PW – potable water

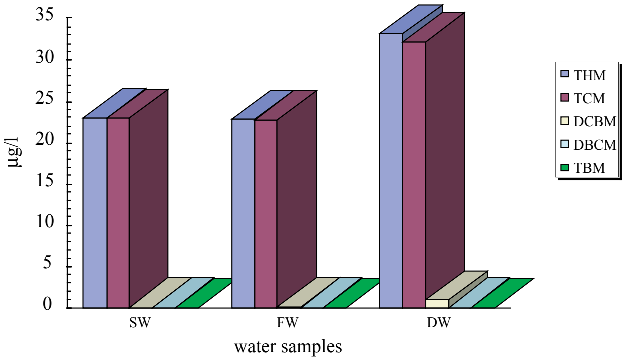

Fig. 2. THMs evolution on Bistrita DWTP steps (pre-chlorination–coagulation–flocculation–settling–filtration–clorination/disinfection)

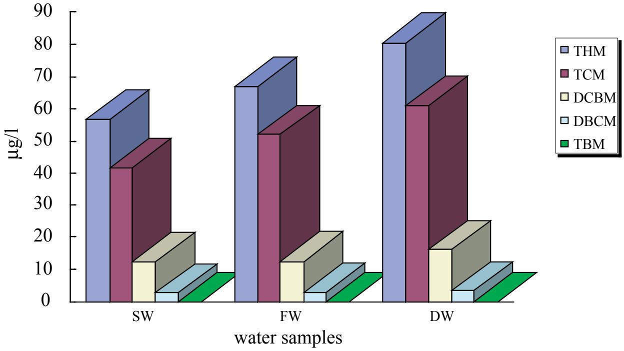

Fig. 3. THMs evulation on Tulcea DWTP steps (pre-chlorination–coagulation–flocculation–settling–filtration–clorination/disinfection)

Table 1. The incidence of THM in drinking water. Raw water sources – surface water (barrier lakes/rivers)

No	Treatment plant	Water company	Raw water source	Trihalomethanes (µg/l)				
				THM	TCM	DCBM	DBCM	TBM
1	Bucecea	Apa Grup Botosani	barrier lake – Bucecea/Siret	36.37/37.65	33.23/34.89	3.14/2.48	0/0.25	0/0.02
2	Catamarasti		barrier lake – Bucecea/Siret	18.83	17.45	1.24	0.12	0.01
3	Saveni		barrier lake – Negreni	**121.08**	93.97	23.03	3.28	0.8
4	Stefanesti		barrier lake – Stanca costesti	6.2/17.1	4.9/16.04	1.04/0.94	0.19/0.08	0/0
5	Santamarie Orlea	Apa Prod Deva	barrier lake – Hateg	**545.14**/37.16	544/36.28	0.98/0.82	0.14/0.02	0.02/0
6	Tarlung-Sacele	Apa Brasov	barrier lake – Tarlung	29.73/28.34	19.61/25.56	6.03/2.51	3.14/0.27	0.95/0
7	Bogata-Rupea		barrier lake – Dopca	17.98/37.37	17.38/32.5	0.31/4.7	0.17/0.87	0.1/0.3
8	Timisoara (U2-4)	Aquatim	Bega river	17.15/33.25	10.47/28.85	5.18/4.35	1.5/0.66	0/0.09
9	Bistrita	Aquabis	Bistrita river	26.5/33.16	25.7/32.19	0.56/0.94	0.16/0.03	0.08/0

Table 2. The incidence of THM in drinking water. Raw water source – the Danube river

No	Treatment plant	Water company	Trihalomethanes (µg/l)				
			THM	TCM	DCBM	DBCM	TBM
1	Drobeta Turnu Severin	Secom Drobeta	14.97/27.49	11.62/20.76	2.57/5.62	0.78/1.02	0/0.09
2	Galati	Apa Serv	32.3/63.83	17.7/47.7	10.4/12.86	2.6/2.9	1.5/0.24
3	Cernavoda	Detacan	27.5/89	22.1/71.36	4.6/14.75	0.8/2.76	0/0.13
4	Tulcea	Aqua Serv	80.63/59.88	61.05/42	16.24/14.35	3.34/3.21	0/0.03

Table 3. The incidence of THM in drinking water. Raw water sources : GW–groundwater, BIW–bank infiltration water

No	Treatment plant (TP)	Water comp any	Raw water source	Trihalomethanes (µg/l)				
				THM	TCM	DCBM	DBCM	TBM
1	Timisoara (U1)	Aquatim	GW	37.75	4.21	2.68	10.44	20.42
2	Timisoara (U5)		GW	52.88/16.13	3.19/6.59	8.28/2.32	25.41/3.96	16/3.26
3	Geoagiu–Folorat	Apa Prod Deva	GW	32.27	24.23	6.86	1.55	0.63
4	Geoagiu–Clocota		GW	32.36	26.7	2.82	2.28	0.56
5	Baniu–Roscani		GW	17.98/18.37	17.38/17.86	0.31/0.37	0.17/0.11	0.11/0.03
6	Brad–Criscior		GW	38.12/39.42	37.05/38.47	0.82/0.84	0.23/0.11	0.01/0
7	Sanpetru–Hunedoara		GW+Hobita barrier lake	58.02/50.88	56.24/49.21	1.30/1.61	0.38/0.06	0.09/0
8	Galati–Filesti	Apa Serv	GW	22.91/44.34	17.85/24.06	1.58/4.88	2.18/7.43	1.29/7.97
9	Turda	RATACFL Turda	GW	31.61/35.37	30.73/32.27	0.41/1.72	0.47/1.17	0/0.21
10	Botosani–Darabani	Apa Grup Botosani	BIW	6.8	4.2	1.57	0.91	0.09
11	Satu Mare–Martinesti	Apa Serv Satu Mare	GW	1.15/19.8	0/18.22	0.68/0.54	0.47/0.32	0/0.1
12	Tulcea–Bogza	Apa Serv Tulcea	GW	13.16	10.15	0.38	0.17	2.46
13	Oradea (U1,U3) the Cris river – right bank	Compania de Apa Oradea	BIW	140.44/27.78	139.9/26.64	0.98/0.83	0.54/0.27	0/0.04
14	Oradea (U2, U4) the Cris river – left bank		BIW	2.71/23.68	1.08/22.96	1.07/0.53	0.56	0/0

Table 4. Evolution of THMs in drinking water along the route storage – distribution – consumer. Raw water source underground water (U1 – DWTP Timisoara)

No	Trihalomethanes (μg/l)	ST_i	DN_i	C
1	THMs	22.59/29.69	46.98/51.7	85.56/97.41
2	TCM	9.09/9.1	9.27/9.52	26.87/37.65
3	DCBM	1.96/1.99	3.06/3.3	4.75/4.5
4	DBCM	4.16/6.3	11.38/12.97	17.23/17.99
5	TBM	7.38/12.3	23.27/25.91	36.71/37.27

THM – trihalomethanes; TCM – trichloromethane; DCBM – dichlorobromomethane; DBCM – dibromochloromethane; TBM – tribromomethane; ST_i – storage tanks inlet; DN_i – distribution network inlet; C – consumer.

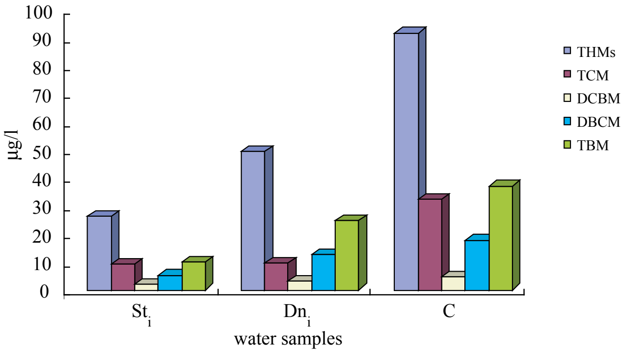

Fig. 4. THMs evulation on Timisoara DWTP steps (along the route storage – distribution – consumer) – average values

The variation domains of disinfection by-products in the drinking water are the following:

• THMs less than 50% of MAC (1.15-47.74 μg/l), for 79% of total analyses (47 samples);

• THMs higher than 50% of MAC, but under 100 μg/l for 15% of the investigated samples (50.88-89 μg/l);

• THMs above MAC for 6% of performed analyses (121-445 μg/l).

Among all THMs, chloroform is the main compound, representing between 55-99% of global concentration of THM. Also, for 27% of analysed samples, chloroform is higher than 30 μg/l (TTHM < 50 μg/l).

Two exceptions are registered for DWTPs U1 and U5 (Timisoara) where the representative disinfection by-products are brominates (dibromochloromethane and bromoform). The occurrence of brominates substances in potable water (DBCM + TBM = 78-80% of THMs) is due to the presence of bromide ions in ground water ($Br^- \leq 1.6$ mg/l).

The organic matter (TOC) concentrations in the natural resources are variable between 0.68-6.81mg C/l. The highest values are corresponding to the raw water samples collected from barrier lake Orlea (TOC = 6.81 mg/l; DWTP – Santamarie Orlea – Deva) and barrier lake Negreni (TOC = 5.61 mg C/l; DWTP – Saveni – Botosani), which have generated THM concentrations exceeding MAC. It must be mentioned that high value of THMs in respect with the MAC (100 µg THM/l) may be associated also with low initial TOC value (less than 2 µg C/l), emphasising the influence of organic matter nature in THM generation (TOC = 140.44 µg C/l; DWTPs Oradea – bank infiltration water as water supply). Thus, it is obvious that the nature of organic species is more important than the concentration of level (TOC value) in the generation of chlorination by-products.

Regarding the evolution of THMs when two chlorination steps are used, the enhancement of THMs level in the water along the treatment flow steps was registered (Figs 1-3).

The same increasing behaviour of THMs was observed for the drinking water sampled on the route: storage tanks – distribution network – consumer (Table 4, Fig. 4).

CONCLUSIONS

The study has evaluated the drinking water quality from the point of view of THMs incidence, in 27 DWTPs of Romania, which are using surface water (rivers, barrier lakes) and groundwater (including bank infiltration water) for water supply. The investigation results can be summarised as follows:

- The majority of the drinking water samples representing 94% from all the analysed assays are in compliance with the requirements of the Romanian/European legislation regarding the THMs (MAC = 100 µg/l);
- Pre-chlorination may generate THMs levels exceeding the MAC, in the presence of organic matter (high TOC values = 5-7 mg C/l) or precursors, with high production of THMs even if TOC value is less than 2 mg C/l, which confirms the importance of organic species nature in THMs generation;
- Chloroform is the mainly by-product formed by chlorination (55-99% of THMs) in the absence of bromide ions;
- The presence of bromide ions (not stipulated parameter in the specific legislation) at low concentration level ($Br^- < 1.6$ mg/l) enhances the generation of brominates compounds (≤ 80% of THMs) in the drinking water;
- Tap water (at consumer) could have THMs levels higher than the concentrations determined at DWTPs (storage tanks) due to the development of specific reactions between chlorine in excess and organic matter into distribution network.

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