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DISTRIBUTION OF ORGANOCHLORINE POLLUTANTS IN THE SOMES RIVER BASIN

PhD Thesis Abstract

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Contents

PERSONAL CONTRIBUTIONS

Introduction

The community aquatic medium must be protected against pollution, especially against the one caused by persistent, toxic and bio-acumulable substances, by simultaneous actions of states governments and different medium protection agencies from all over the world.

The purpose of this thesis was the monitoring of the distribution of organochlorine derivatives produced by industrial and agricultural activities in the Somes river basin, Somesul Mare River respectively.

The selected analytical method was the gas chromatography (GC) with electron capture detector.

The concentration maxima of organohalogen derivatives in national surface water are prescribed within the framework of Water 2000/60/EC regarding the environment quality standards- domain water-part A.

Pollution by discharging different dangerous compounds such as organohalogen derivatives and other compounds from List I (Within the framework UE/ 464/ CEE, transposed in the Romanian legislation by HG 351/ 2005), must be eliminated.

The study performed during 2006-2008, contains monitoring of organohalogen derivatives in the water of Somes River in the area of towns Jibou, Beclean and Dej.

The water samples were collected monthly from river Somes in the established monitoring points situated upstream and downstream the towns mentioned above, as well as from the water treatment plants situated in the area.

Organohalogen derivatives such as: chloroform, methylene chloride, carbon tetrachloride, trichloroethylene, tetrachloroetylene and trichlorobenzene were identified. Among trihalomethanes, chloroform appeared in higher amounts, as compared to bromodichlromethane, chlorodibromomethane or bromoform. The recorded values for trihalomethanes are situated in the permissible limits according to present legislation.

These compounds might result from industrial activities performed in the studied area, a fact which appears as an alarming situation.

PERSONAL CONTRIBUTIONS

Chapter IV. Water sampling from Somes River and organochlorine derivatives analysis method

4.1. Presentation of geographical area

Fig.1. The map of the Somes river basin

The studied area is part of the Somes river hydrographical basin. Localization of the water treatment plants is highlighted in figure 1. Somesul Mare and Somesul Mic rivers traverse rapidly the mountain area and their confluence is situated near Dej.

The study of the water quality is of maximum importance due to the fact that Somesul Mare river is the source of drinking water for many large towns from the area: Dej, Beclean, Nasaud.

4.2. Description of the sampling pattern employed for the determination of organoclorine derivatives produced during the water disinfection process in the treatment units adjacent to Somes River

4.2.1. Water sampling at the water treatment plant S.C. Someş S.A. Dej

Drinking water is produced at water treatment plant S.C. Someş S.A. Dej according to the steps shown in Figure 2.

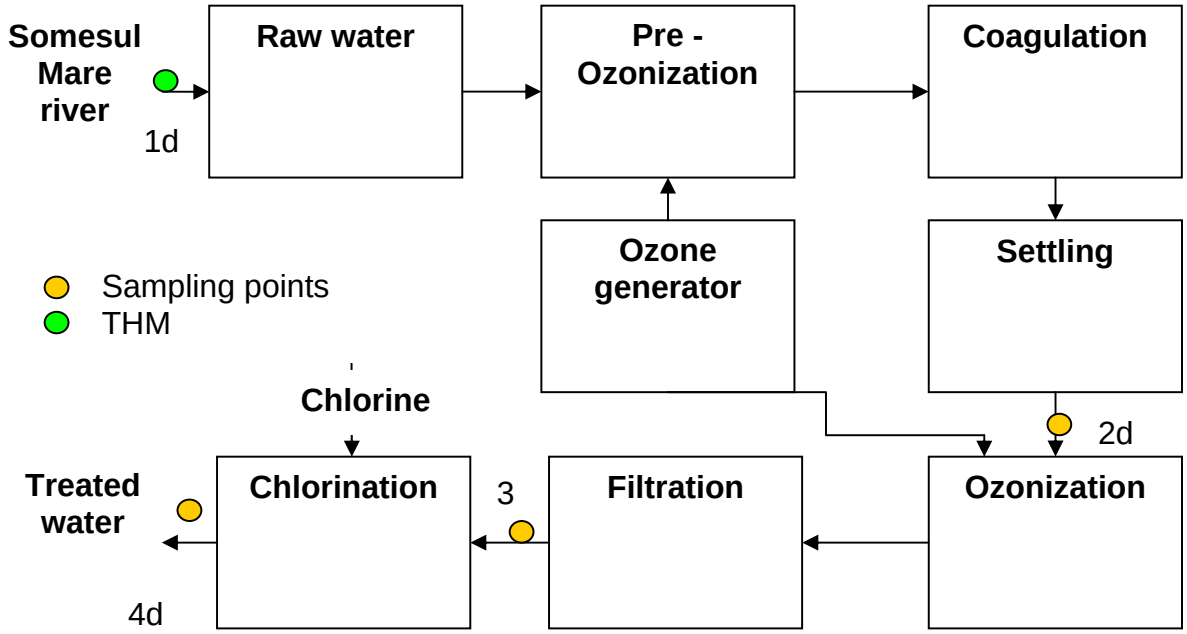


Fig. 2. Water treatment and sampling points at S.C. Someş S.A. Dej

4.2.4. Determination of organochlorine derivatives produced during the disinfection process – trihalomethanes

The water samples were qualitatively and quantitatively analyzed by GC method using a gas chromatograph *Trace GC Ultra* with electron capture detector (^{63}Ni). Best results were obtained when column type TR-V1 cyanopropylphenyl polysiloxane, 30 m x 53 mm, 3 □m thick was employed.

The carrier gas was nitrogen. The operation conditions are described in table 4.2.

The standard solutions of trihalomethanes were kept into the refrigerator at constant temperature of 4 □C, avoiding light exposure.

The calibration curves were obtained using standard solutions with concentrations in the range 1-100 µg/l for each compound.

Chapter.VI. Organochlorine compounds identified in the water of Somes River

6.1. Organochlorine compounds identified in the water samples from Somes River collected in the Jibou town area

Figure 3 shows the gas chromatogram obtained from a water sample collected in the year 2007 in the Jibou town area.

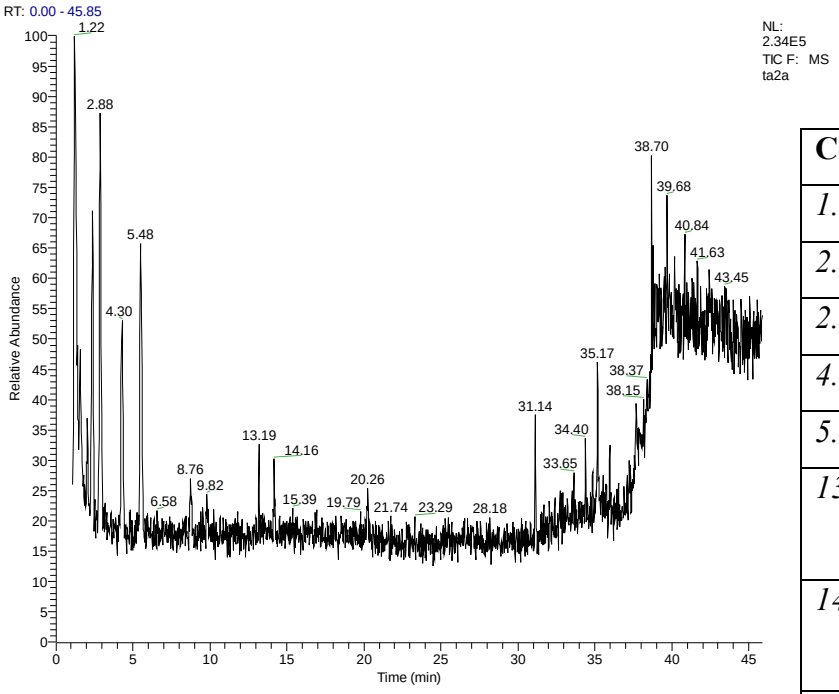


Fig.3. Gas chromatogram obtained from a water sample collected in the year 2007 in the Jibou town area and the assignment of water pollutants based on retention times.

Compound	Retention time
1.22	Chloroform
2.37	Benzene
2.88	Triclhoroethylene
4.30	Methylene chloride
5.46	Tetrachloroethylene
13.19	*Cis*-1,3-chloropropylene
14.16	*Cis*-1,3-dichloropropane
31.14	1-Decane
35.17	*n*-Decanoic acid 2,3-dichloro benzenamide
38.70	*n*-Decanoic acid

Samples were collected from Somes River into two sampling points separated by a distance of 6 km and situated downstream Jibou. Variations of the concentrations of organochlorine derivatives (trichloroethylene, tetrachloroethylene and dichloromethane) were observed as follows:

-highest concentrations were recorded during summer months June and July.

-increasing concentrations were observed from winter to summer, than concentrations are decreasing proportionately.

-concentrations of trichloroethylene, tetrachloroethylene and dichloromethane in sampling point 2 appear as half of the concentrations in the sampling point 1.

Quantitative determinations were performed using water samples collected from Somes River in 6 sampling points situated at 10 km downstream the town Jibou during the month of may 2007. Highest concentrations were recorded for trichloroethylene, then carbon tetrachloride followed by tetrachloroethylene, the rest of organochlorine derivatives being under the detection limit.

During the months of May and July 2007, organochlorine pesticides were determined in the water samples collected in the Jibou town area. Higher concentrations were recorded for: *pp*-DDE,– 0.105 [μg/l], α-HCH 0.094 [μg/l] and γ-HCH – 0.18 [μg/l], while aldrin and dieldrin were not detected.

Partial conclusions:

In the Jibou town area were identified:

-high concentrations of trichloroethylene, tetrachloroethylene and dichloromethane

-low concentrations of chloroform

-very low concentrations of organochlorine pesticides HCH, DDE, DDT

-trichlorobenzene, pentachlorobenzene and hexachlorobenzene were not detected.

The organochlorine pollutants determined in low concentrations in these water samples may occur due to industrial and agricultural activities as well as drinking water disinfection process.

6.2. Organochlorine compounds identified in the water samples from Somes River collected in the Beclean town area.

Figure 4 shows the gas chromatogram obtained from a water sample collected in the year 2007 in the Beclean town area.

The study was performed during the year 2007 for samples collected from Somes River in 6 points: 3 points situated on the right river bank and 3 points situated on the left river bank. The distance between two sampling points was 2 meters. The main organochlorine derivatives identified were chloroform, trichloroethylene and tetrachloroethylene. In some cases (*e.g.* chloroform) the variations from one sample to another are more than 50%.

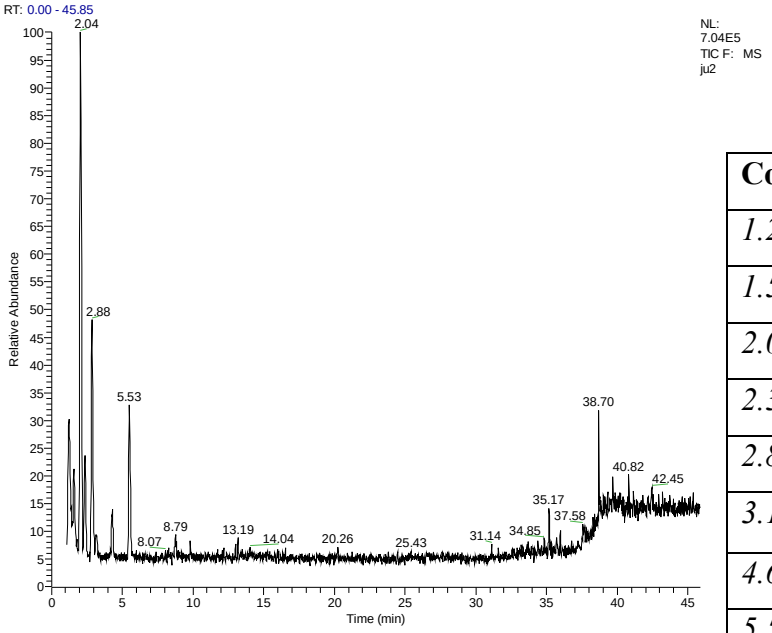


Fig.4. Gas chromatogram obtained from a water sample collected in the year 2007 in the Beclean town area and the assignment of water pollutants based on retention times.

Compound	**Retention time**
1.25	Chloroform
1.59	Methylen Chloride
2.04	Tetrachloroethane
2.35	Carbon tetrachloride
2.88	Bromodichloromethane
3.14	α,α-Dichloroacetone
4.62	Toluene
5.53	2,6-dichlorofluorobenzene
8.79	Ethyl benzene
35.17	2,3-Dichloro-benzenamine
38.70	1,6-Dichloro-6-nitroaniline

When values obtained during the month of June are compared to those obtained in December important modifications were observed as follows:

-methylenechloride concentrations increased up to 100%

-trichloroethylene, tetrachlorolethylene and chloroform concentrations increased up to 35 %.

Partial conclusions:

In the Beclean town area were identified:

-huge modifications of organochlorine derivatives concentrations related to season variations (higher values were determined during summer);

-pesticides containing organochlorine derivatives were identified in small amounts, such as: α-HCH 0.042 -0.069 µg/l, γ-HCH 0.095- 0.025 µg/l, *pp*-DDE 0.024-0.17 µg/l, *op*-DDT 0.016- 0.18 µg/l and *pp*-DDT 0.088 - 0.093 µg/l.

The organochlorine pollutants determined in low concentrations in these water samples may occur due to industrial and agricultural activities as well as drinking water disinfection process

6.3. **Organochlorine compounds identified in the water samples from Somes River collected in the Dej town area**

Figure 5 shows the gas chromatogram obtained from a water sample collected in the year 2007 in the Dej town area.

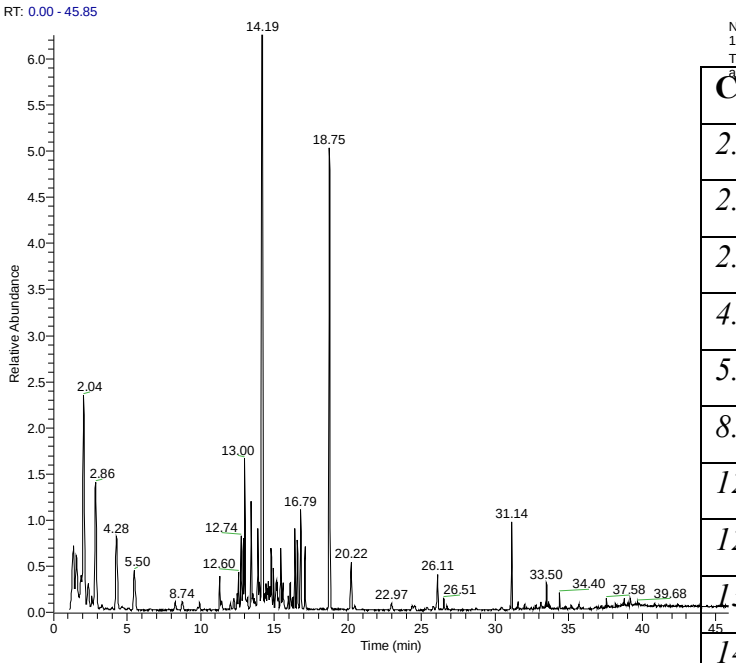


Fig.5. Gas chromatogram obtained from a water sample collected in the year 2007 in the Dej town area and the assignment of water pollutants based on retention times.

Compound	**Retention time**
2.04	Chloroform
2.37	Benzene
2.86	Trichloroethylene
4.28	Toluene
5.50	Tetrachloroethylene
8.74	*o*-xylene
12.60	*Cis*-1,3-dichloropropylene
12.74	*Cis*-1,3-dichloropropane
13.00	1-dodecane
14.19	*Cis*-1,2-dichloroethene
16.79	Dodecanoic Acid
18.75	Chloroxine
20.22	Chloromethylsilane
26.11	2-celoro-1,3-butadiene
26.51	Chloroacetylaldehyde
31.14	Bis-2-chloroethyleter

Variable concentrations of chloroform were recorded during the year 2007 in the Dej town area. Great differences of the detected concentrations were observed between the two sampling points situated upstream and downstream Dej. During the period may-October 2007 higher concentrations were recorded downstream Dej (with a maximum recorded in august, a value which represents the double of the upstream concentration)

Downstream concentrations of trichloroethylene, tetrachloroethylene and carbon tetrachloride were also higher as compared to upstream values all over the year 2007. For instance, the maximum concentration of carbon tetrachloride 21.14 µg/l was recorded in august 2007 (if compared to the maximum permissible value 12 µg/l, an alarming situation may occur).

Chapter. VII. Pollution with organochlorine compounds in the Somes River, induced by the Industrial platform Nord Dej –Cellulose and Paper Plant

The increased values recorded for chloroform concentrations downstream Dej might be a result of the industrial activities performed on the Industrial platform Nord Dej where a Cellulose and Paper plant is located. Due to the fact that the waste water produced on this industrial platform is treated at the biological treatment unit Urisor and then discharged in the river Somes, I decided to monitor this area in order to identify the organochlorine derivatives which might appear as water pollutants.

The technological processes for cellulose and paper production consist in the following steps:

-Wood preparation (pealing, hashing, and sorting)

-Boiling of the hashing in alkaline solution

- Sorting of the cellulose paste

- Washing of the cellulose paste

-Whitening of the cellulose by treatment with chemical reagents which remove lignin and bleaching

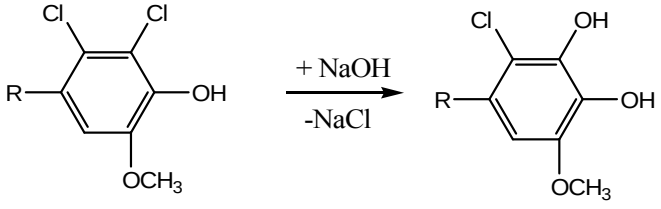
-Paper installation

-Cellulose dehydration installation

Cellulose Whitening

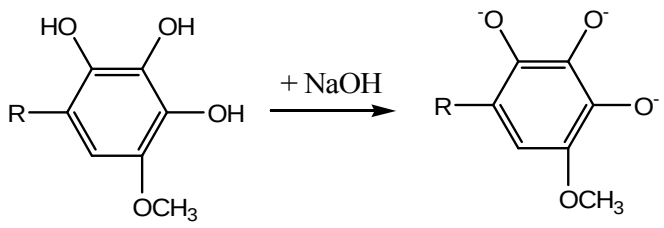
The whitening of the cellulose paste is accomplished using a conventional technology based on treatment with chlorine. Cellulose is treated with chlorine, followed by alkaline extraction and treatment with chlorine and chlorine dioxide.

Chlorination of lignin takes place by addition of halogen to the double bond situated in the propyl side chain and/or by electrophilic substitution of the aromatic ring (in position 5 and 6). The chlorinated lignin is partially soluble in water and for a better extraction in water, the cellulose is treated with diluted alkaline solutions, when 60-90% of the chlorine is substituted (scheme 1) and the ionization of the acidic phenol groups may occur.



Scheme 1

The NaOH solution employed in the extraction process neutralizes the acidity of the phenol groups generating sodium phenolates (scheme 2), which are the most soluble states of lignin.



Scheme 2

The oxidation may determine the elimination of the carbonyl group from the alkyl side chain as carbon dioxide.

The whitening process must contain at least one oxidation step, followed by washing of the solubilized lignin.

Other whitening reagents are: chlorine dioxide (which reacts slowly with lignin and the temperature of the process must be increased), sodium hypochlorite (which generates oxidation products such as carboxylic acids and CO2), oxygen and hydrogen peroxide (the most environmental friendly processes).

This chlorination process was suspected to produce waste water containing organochlorine derivatives which, by discharging into the river, could create pollution downstream. Even though the monitoring previously performed did not revealed that this installation is the unique source for pollution in the area, evidence was brought during the 2 weeks of scheduled stop period of this installation. Thus, during the month of July, samples of water were collected from the river, before and during the stop of this installation. The results of the monitoring process shown in figure 5 indicate a tendency of reduction of chloroform concentrations after the 15th day of the period; during the period when the installation was stopped the chloroform concentration dropped from 90-70 µg/l to 60-40 µg/l.

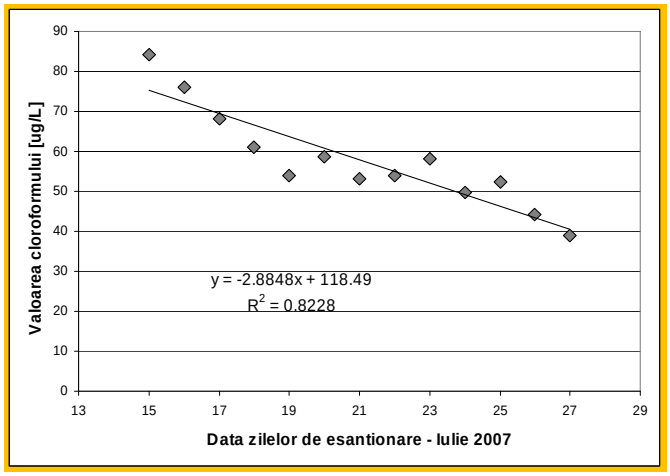


Fig.5-Variation of chloroform concentration [µg/l] downstream Dej, in July 2007 during the period when the installation of cellulose and paper was stopped.

The same tendency was observed for tetrachloroethylene and trichloroethylene as well (shown in figure 6).

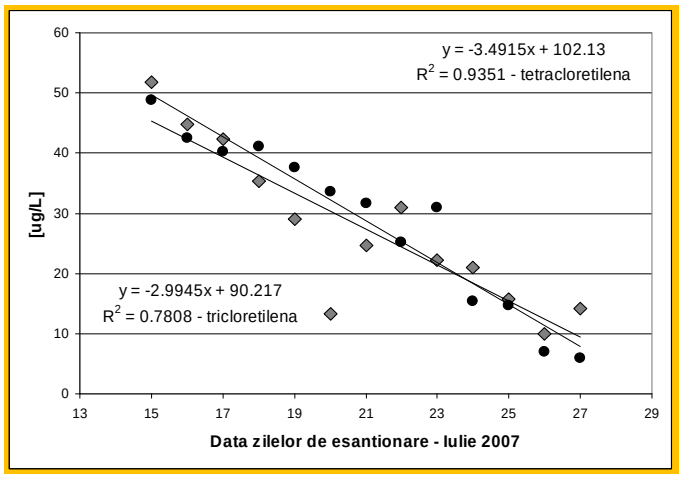


Fig.6 - Variation of tetrachloroethylene and trichloroethylene concentrations [µg/l] downstream Dej, in July 2007 during the period when the installation of cellulose and paper was stopped.

PARTIAL CONCLUSIONS

The monitoring in Dej area were shows:

-higher concentrations of organochlorine derivatives as compared to other monitored areas

- trichloroethylene, tetrachloroethylene and chloroform concentrations are below the permissible maxima values, while carbon tetrachloride concentrations are slightly above these values.

- the differences between the concentrations of organochlorine derivatives upstream and downstream Somes river, indicate that the industrial activities performed on the industrial platform Nord Dej, in the cellulose and paper plant respectively, produce a small polluting effect additional to agricultural activities.

Chapter VIII. Formation of trihalomethanes in the water treatment plant and in the drinking water distribution network in Dej town area.

8.1. Chlorine dosage effect

Previous studies demonstrated that the main factors favoring the THM formation are: the dosage of chlorine at the water treatment plant, the concentration of chlorine in the distribution system, the concentration and type of organic precursors in the treated water, the contact time, and the water pH.

The formation of THM was analyzed at the Water Treatment Plant and in the distribution system in Dej town area.

Organic compounds present in water (TOC) can react with chlorine following a complex reaction mechanism. The formation of trihalomethanes (THM) might be the crucial reaction step but the reactions kinetics (such as reaction rate, rate constant, order of reaction) are difficult to determine. A general reaction is presented in scheme 3

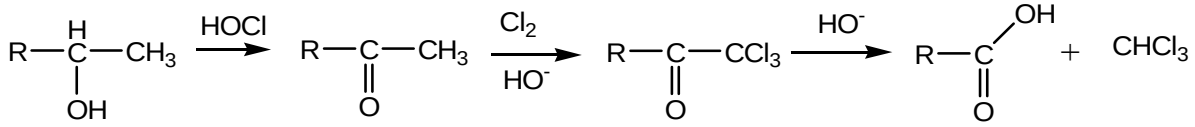
$$3\,A + B \xrightarrow{k_n} C$$

Where: A - HOCl; B - TOC; C – THM; k_n - the rate constant

Scheme 3

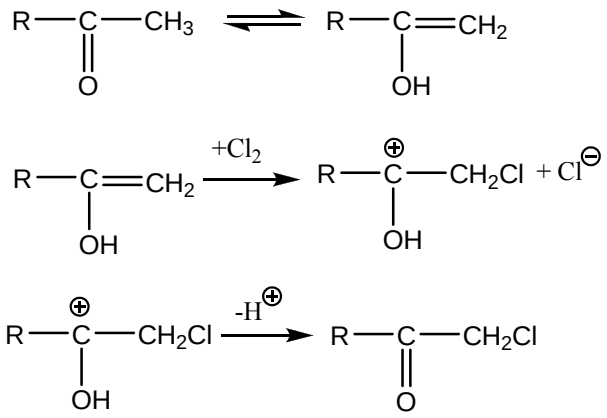
In alkaline solutions, the formation of chloroform is based on haloform reaction mechanism presented in scheme 4

The α methyl ketone formed by oxidation of organic compounds is chlorinated stepwise to trichloromethyl-ketone which undergoes a nucleophilic acyl substitution in the presence of a base, thus generating the carboxylic acid and chloroform.



Scheme 4

In acid solutions the chlorination of ketones proceeds by addition of chlorine to the intermediate enol form as shown in scheme 5.



Scheme 5

The formation of trihalomethanes becomes possible only in alkaline solutions.

The drinking water source for Dej town area is the water of Somesul Mare River. Water is collected from Mica barrage situated at 1 km distance from the confluence of rivers Somesul Mic and Somesul Mare.

In the water treatment plant Dej, the disinfection of water is performed with ozone and further treatment with chlorine is required for a better permanence in the distribution network. The chlorine dose is 0,5-0,9 mg/ l.

During this study samples were collected monthly from the following sampling points:

-raw water tank

-preozonized and filtrated water tank

-chlorinated water tank

-distribution network and domestic tap water

Highest concentrations of trihalomethanes in the water samples were recorded for chloroform in the distribution network (up to 80µg/l). Bromodichloromethane and dichlorobromomethane concentrations were situated below 6 µg/l.

A direct correlation was observed between the increasing chlorine dose and the formation of THM (THM concentration respectively). Figure 7 shows the relationship between the chloroform concentration and the chlorine dosage at the water treatment plant.

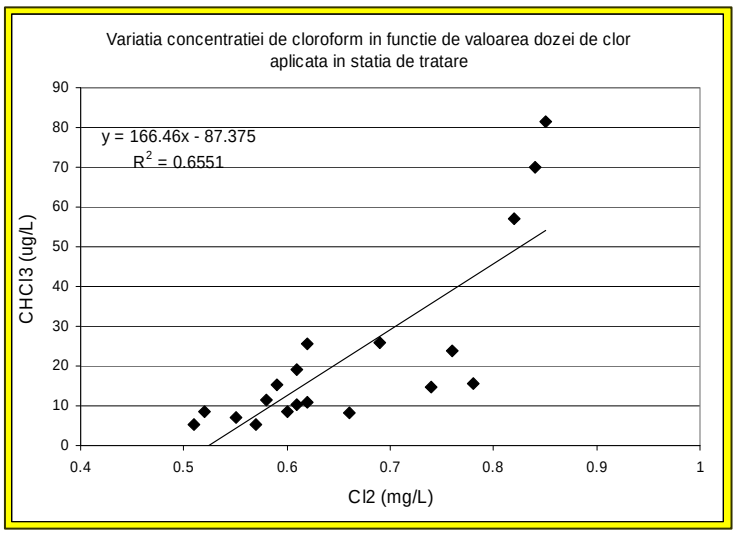


Fig.7-Correlation between chlorine dosage at the water treatment plant and chloroform concentration in the water samples

The total organic compounds concentration in the water has a crucial role in the formation of trihalomethanes. For this study, the content of organic compounds in water samples was determined using the standard method of oxidation with KMnO4 in acid solution.

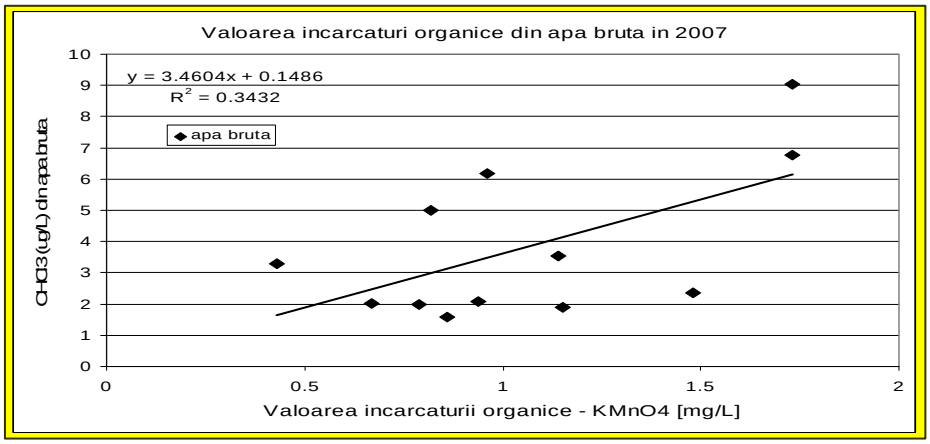


Fig. 8-Correlation between the detected chloroform concentrations and the total organic compounds content in raw water samples collected in 2007 from Somes River in Dej town area.

From figure 8 a direct relationship between the organic compounds content in raw water samples and the chloroform concentration detected in the distribution network can be observed.

Longer reaction time favors the formation of higher amounts of chloroform. As it can be seen from figure 9, higher amounts of chloroform appear in the water samples collected in different sampling points situated on the flow chart as follows: raw water tank (6,47µg/l), preozonized and filtrated water tank (8,54 µg/l), chlorinated water tank (27,62µg/l), after four and a half hours, when the water riches the entrance in the town distribution network the concentration was 48,95µg/l and after 12 additional hours the concentration of chloroform was 61,07µg/l.

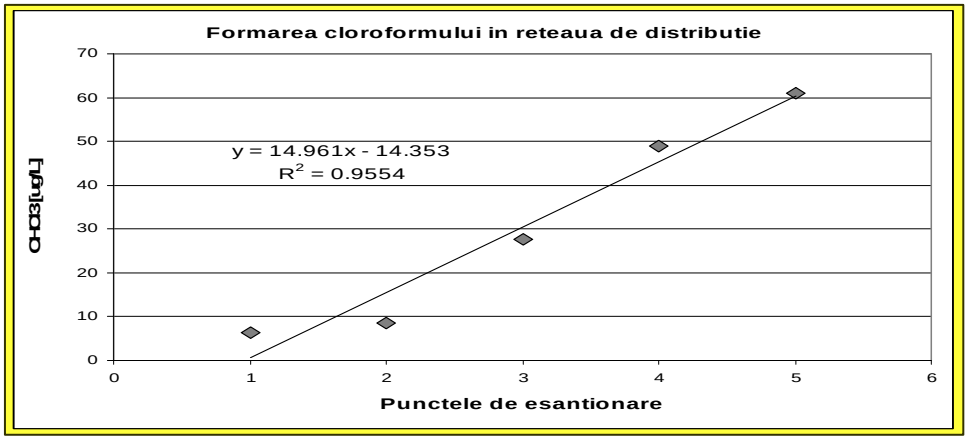


Fig. 9-Formation of chloroform in the water treatment plant and distribution network in the Dej town area

PARTIAL CONCLUSIONS

Formation of THM is influenced by the following factors: chlorine dosage for efficient disinfection, the distance completed by the water in the distribution network, the contact time, the total organic compounds content and the seasonal variations.

Chapter. IX. General conclusions

Monitoring of organohalogen derivatives in the water of Somes River in the area of towns Jibou, Beclean and Dej was performed during 2006-2008.

The water samples were collected monthly from the established sampling points situated in the water treatment plants area and from the river water upstream and downstream the towns Jibou, Beclean and Dej.

The water samples were qualitatively and quantitatively analyzed by GC method using a gas chromatograph Trace *GC Ultra* with electron capture detector.

Several organochlorine derivatives such as: chloroform, methylenechloride, carbon tetrachloride, trichloroethylene, tetrachloroethylene, trichlorobenzene, were detected in concentrations below the permissible maximum values according to legal standards. Slightly higher values were recorded for carbon tetrachloride concentration in Dej area. These organochlorine compounds may occur as a result of human industrial and agricultural activities in the area, which becomes an alarming signal.

Among the trihalomethanes formed during the disinfection of water with chlorine, the chloroform was detected in most cases in higher amounts as compared to bromodichloromethane, chlorodibromomethane or bromoform. The THM concentrations in the drinking water distribution network are situated below the permissible maximum values according to legal standards

Pollution by discharging different dangerous compounds such as organohalogen derivatives and other compounds from List I within the framework UE/ 464/ CEE, transposed in the Romanian legislation by HG 351/ 2005, must be eliminated.

PUBLISHED PAPERS

1.M.H. Kovacs, D. Ristoiu, Sidonia Vancea, L. Silaghi-Dumitrescu*: Volatile organic disinfection by products determination in distribution system from Cluj-Napoca, STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, LIV*, 2009, vol 3, p. 107 – 117.

2. Dumitru Ristoiu, Urs von Gunten, Aurel Mocan, Romeo Chira, Barbara Siegfried, Melinda Haydee Kovacs *and* Sidonia Vancea*: Trihalomethane formation during water disinfection in four water supplies in the Somes river basin in Romania, Environmental Science and Pollution Research,* **2009***, vol. 16, supl. 1.*

3.Dumitru Ristoiu, Melinda-Haydee Kovacs, Iovanca Haiduc, Sidonia Vancea: *Disinfection efficiency - Trihalomethanes formation after chlorination process, Water environment journal,* **2008***, p. 146 – 152.*

Poster presentations to scientific manifestations:

1.''Contamination of drinking water with organochlorine derivatives as a result of disinfection process''-*XXIX Romanian Chemistry Conference* 4-6 oct. **2006**, Caciulata, Romania
Sidonia Vancea, Aurel Mocan, Romeo Chira, Luminita Dumitrescu, Dumitru Ristoiu,*Books of abstracts*, 2006,p.439

2.''The evaluation of Spatial Fluctuations and Temporal Variability in Estimated Levels of THMs in Drinking Water"-*International Conference of the Balkan Physical Union*, 22-26 aug.**2006**, Istanbul Turkey

D.Ristoiu, I.Haiduc, M.Culea, A.Mocan, R.Chira and S.Vancea, *Book of Abstracts,* 22-26 aug.2006, Istanbul

3..''Organochlorine identification in waste water and sediments Dej city''-*International Conference Environment Natural Sciences Food Industry*-1 ST Edition Baia Mare-Romania, **2007**.

Sidonia Vancea, Melinda Kovacs, Luminita Silaghi-Dumitrescu, Dumitru Ristoiu,*Conference proceedings*, nov.2007, Baia Mare, p.174

4.''Disinfectant decay and disinfection by-products formation model development chlorination by-products'', International Conference Environment Natural Sciences Food Industry-1 ST Edition Baia Mare-Romania, 2007.

Kovacs Melinda-Haydee, Vancea Sidonia, Dumitru Ristoiu, *Conference proceedings*, nov.**2007**, Baia Mare, p.67.

5.''Distribution of organochlorine solvents in the surface water from Cluj district" - *XXX Romanian Chemistry Conference* 8-10 oct. **2008**, Caciulata, Romania

Melinda-Haydee Kovacs, Sidonia Vancea, Luminita Silaghi Dumitrescu, Dumitru Ristoiu, *Books of abstracts*, **2008**, p.373.