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# FORMATION OF THE HALOACETIC ACIDS DURING OZONATION AND CHLORINATION OF WATER IN WARSAW WATERWORKS (POLAND)

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**Abstract**—The results of the study of the HAAs formation in Water Works in Warsaw, Poland are presented. Water taken from Zegrzyńskie Lake is characterized by elevated content of humic substances and algae bloom in hot seasons. The water is ozonated and chlorinated. The study was performed from October 1995 to November 1996. The water was analyzed on various stages of treatment and the following parameters were determined: HAAs, THMs, DOC, COD, humic substances, UV absorbance, color and temperature. The big increase of HAAs concentrations occurred after water chlorination, up to 120  $\mu$ g/l. In 44% it was DCAA and in 40% TCAA. The highest concentration of HAAs was noticed in May and June, when water temperature was the highest and concentration of organic matter the big gest. The changes of HAAs concentrations with time were similar to those in THMs concentrations.

The laboratory experiments on the water ozonation and chlorination indicated that ozonation has small influence on the HAAs formation.

The study of the HAAs volatization during water boiling showed that removal of HAAs is rather small. © 1999 Elsevier Science Ltd. All rights reserved

Key words-haloacetic acids, water ozonation and chlorination

## INTRODUCTION

Haloacetic acids (HAAs) are formed during the chlorination of organic matter occurring in water taken for the treatment. In general, natural organic matter such as humic and fulvic substances are important precursors of HAAs.

It is generally known that disinfection by-products are formed by-using chlorine as a water disinfectant. The primary group of DBPs formed during the chlorination are the trihalomethanes (THMs). The main representative of this group — chloroform is recognized as a potential human carcinogen. The second most prevalent group of chlorination by-products are the haloacetic acids. Some of them, namely dichloroacetic acid and trichloroacetic acids are potentially animal carcinogens (Clark, 1989). Very large health risk has also bromodichloromethane (BDCM) (Rannung and Ramel, 1997).

Many studies were carried out on disinfection byproducts (DBPs) formation (Summers *et al.*, 1993; Fielding *et al.*, 1987).

It is generally known that formation of DBPs highly depends on the organic matter content

(Pourmoghaddas and Stevens, 1995), but there are many other factors such as organic matter composition and manner of water treatment, especially the use of other disinfectants, i.e. ozone.

Ozonation modifies the structure of organic substances there by influencing the DBPs formation (Calvosa *et al.*, 1991; Yao and Haag, 1997).

Although many studies on the DBPs formation, have been carried out the reduction of the disinfection by-products concentration in tap water is still an important issue (Nieminski *et al.*, 1993).

Peters *et al.* (1991) determined the concentration of HAA in drinking waters in the Netherlands. He found it ranging from trace to  $15 \mu g/l$ .

## Technology of water treatment

Water is taken from Zegrzyńskie Lake. After ozonation, coagulation, pulsators, rapid filter and chlorination water is stored in reservoir in Wieliszew (retention time 2 h). Then water is transported (ca. 5 h) to another reservoir in Bialoleka, is chlorinated again and pumped in to the water network. The scheme of water treatment and the points of water sample intake are shown on Fig. 1.

Water ozonation was done before the coagulation with the doses  $2.4-4.3 \text{ g/m}^3 \text{ O}_3$  (Fig. 4). The contact time was 30-40 min.

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Fig. 1. Technology of treatment. Dotted squares resemble the sampling points.

Water was chlorinated twice, before storage reservoirs (Fig. 1). The average monthly doses of chlorine were changing from 2.1 to  $3.7 \text{ g/m}^3$  Cl (Fig. 4).

After the last storage reservoir the free chlorine residual was between  $0-0.6 \text{ g/m}^3$  and combined chlorine residual was changing between 0.6 to 1.5 g/m<sup>3</sup>.

The study was performed in the period from October 1995 to November 1996. The analysis were done every month. Haloacetic acids were determined and other parameters connected with disinfection by-products such as: humic substances, organic carbon, COD, absorbance UV, color, temperature, chlorine and ozone dosis and THMs.

## Study area

Water supply for Warsaw (population above 1.5 million) is taken from two sources: Vistula River and Zegrzynskie Lake. Zegrzyńskie Lake is the impoundment on Narew River, at the point of Bug River inflows. The Narew River is draining the Mazury Lake Country, so that the water of Zegrzyńskie Lake contains humic substances. Besides that the lake is eutrophic and in hot periods algae blooms occur.

The water from Zegrzyńskie Lake is taken for drinking water supply of Warsaw. By water chlorination the disinfection by-products are formed.

High concentrations of THMs that occurred some years ago were lowered by the introduction of water ozonation. But THMs problems still exist and haloacetic acids (HAAs) were also noticed.

This study was carried out to determine main factors influencing the formation of HAAs in the Warsaw Water Works. The water samples were taken from Zegrzyńskie Lake (raw water), on the various stages of water treatment and tap water (Fig. 1).

#### MATERIALS AND METHODS

#### Method of analysis

A method was developed for the simultaneous analysis of 5 HAAs:

- monochloroacetic acid (MCAA),
- monobromoacetic acid (MBAA),
- dichloroacetic acid (DCAA),
- trichloroacetic acid (TCAA),
- dibromoacetic acid (DBAA).

The haloacetic acids were extracted from water sample with methyl tertiary butyl ether (MTBE). To increase the extraction efficiency a salting agent was added. The extracted compounds were esterified with diazomethane solution to produce methyl ester derivatives. The obtained methyl derivatives were determined using gas chromatography with electron capture detector (ECD).

The detection limit of the method, according to the Standard Methods of APHA *et al.* (1995) is  $0.05-0.08 \ \mu g/l$  depending on the compound. The method was checked for the recovery of HAAs. It was found that the relative standard deviation for the samples with added known amount of HAAs was from 3.9 to 5.9% for river water and mean recovery was 81.3-104.0% depending on the compound.

#### RESULTS

#### HAAs in water of Warsaw Waterworks

The haloacetic acids in raw water (from Zegrzyńskie Lake) were found in trace concentrations; very often there were below detection limit.

Water ozonation gave a very small increase of HAAs, maximum  $1 \mu g/l$  but often no increase was observed.



Fig. 2. Changes of HAAs concentration after different steps of treatment (average value).



Fig. 3. Change of total HAAs in time in the tap water (sampling point No. 6).



Fig. 4. Changes of total HAAs in treated water (sampling point No. 5) in comparison to TOC, water temperature, doses of chlorine and ozone.

A big increase of HAAs was noticed after the first chlorination. The second chlorination gave a further increase (Table 1).

In tap water, concentration of HAAs increased for MCAA, MBAA and DBAA but decreased for DCAA.

The sum of HAAs in tap water was lower than that after the last chlorination (Fig. 2).

Evaluating the content of produced HAAs the findings were as follows:

DCAA-44%, TCAA-40%, MCAA-12%,

MBAA-2%, DBAA-2%, of the 100‰ 5 HAAs.

The concentrations of HAAs were changing with time and depended on the season (Fig. 3). The lowest concentrations were found in winter, namely in January, February and March. The sum of HAAs was below  $13 \mu g/l$ . The highest concentrations occurred in May and June and reached  $120 \mu g/l$ . In early spring and autumn the concentration of

Table 1. Average concentration of HAAs after chlorination ( $\mu$ g/l)

	First chlorination	Second chlorination
MCAA	1.76	3.57
DCAA	13.34	25.55
TCAA	8.18	15.20
MBAA	0.12	0.42
DBAA	0.36	0.45

HAAs was lower,  $(20-50 \ \mu g/l)$ . The changes of the concentration of the individual haloacetic acids were varying with time but in general were the same as for the sum of HAAs.

The changes in HAAs concentration were compared with variations of other water parameters and with the chlorination practice. The highest doses of chlorine were used in April and May and June, when the algae concentrations in water of Zegrzyńskie Lake were the highest. In May and June the contents of HAAs were the highest. It was also noticed that more HAAs was produced at high TOC values but the relationship was irregular.

A very clear relationship was established between the concentration of HAAs and the humic substance content (Fig. 5) and UV absorbance.

In general, more haloacetic acids were produced at higher concentration of organic matter (precursors). In May and June, when the highest concentration of HAAs were observed, the content of the organic matter in raw water was highest also.

A big influence of water temperature on the production of haloacetic acids was observed (Fig. 6). At low water temperature (in January, February and March) a small amount of HAAs was produced; at temperatures, above 20°C (in May and June) the highest concentrations of HAAs were observed.

We may conclude, that the reaction of HAAs formation is highly dependent on temperature and is faster at high temperature.



Fig. 5. Changes of HAAs concentration in relation to humic substances content.

The changes of HAAs concentrations were compared with used doses of chlorine. In the period of high content of HAAs, the bigger doses of chlorine were used.

The relationship between produced HAAs and produced THMs was analyzed (Fig. 7). The changes in concentration of THMs and HAAs were very similar. Water chlorination and ozonization in laboratory conditions

To study the haloacetic acids formation the experiment of chlorination and ozonization experiments were performed. Water from Zegrzyńskie Lake was ozonated during 15, 60, 120, 240 and 360 min. Then water was chlorinated through 24 h and HAAs were determined. Ozone dose was 0.4–



Fig. 6. Relation of the HAAs concentration on temperature.

Table 2. The concentration of HAAs after ozonation and chlorination in laboratory conditions

	Ozonation time (min)					Chlori	ination of	ozonated v	vater after	the time in	n min	
	0	15	60	120	240	360	0	15	60	120	240	360
MCAA, µg/l	n.d.	2.83	4.92	13.40	14.76	27.05	1.73	2.67	8.28	11.43	38.12	54.73
MBAA, $\mu g/l$	n.d.	n.d.	0.04	0.04	0.11	0.24	0.08	0.34	0.48	0.24	0.22	0.06
DCAA, µg/l	0.14	0.35	0.46	0.58	0.56	0.49	54.83	54.46	57.06	58.98	39.92	39.44
TCAA, $\mu g/l$	0.06	0.15	0.26	0.29	0.37	0.59	0.97	4.10	3.57	2.39	1.23	1.23
DBAA, $\mu g/l$	n.d.	0.07	0.07	0.07	0.29	0.51	n.d.	n.d.	n.d.	0.21	0.21	0.21
Sum HAAs, $\mu g/l$	0.20	3.40	5.75	14.38	16.09	28.88	57.61	61.57	69.39	73.25	79.70	95.67

10.3 mg/l O<sub>3</sub>, chlorine dose 3-5 mg/l Cl<sub>2</sub> and chlorine residual  $\geq 0.5$  mg/l Cl<sub>2</sub>. The results are shown in Table 2.

*MCAA*. During ozonation the chloroacetic acid was produced, up to  $27 \mu g/l$  after 360 min. The chlorination of ozonated water sharply increased the content of HAA. After 360 min the process of formation was not finished.

*DCAA*. After ozonation only trace concentrations of HAAs were found. The chlorination produces high content of the acid, up to  $54 \mu g/l$ . It was noticed that with longer ozonation time, the amount of produced DCAA was decreasing.

*TCAA*. The ozonation gave only trace amount of acid. The chlorination produces small content of the acid, up to  $4 \mu g/l$ . The longer ozonation time, the lower concentration of produced TCAA was noticed.

*MBAA*. The ozonation produced only trace amount of the acid, the chlorination also very small content. With longer ozonation time the produced MBAA content was lower.

*DBAA*. The ozonation and the chlorination produced only trace amount of that acid.

Summarizing we can state, that after ozonation only MCAA was found at significant content, other acids were at trace level.

Theoretically the adding of ozone can not be the reason for chloroacetic acid formation. It could be explained by the oxidation process of chloride to hypochlorite ion (Grguric *et al.*, 1994) by the high dose and long contact time of ozone. The reaction may occur

$$O_3 + Cl^- \rightarrow O_2 + OCl^-$$

The chlorination produced high amount of MCAA and DCAA, other acids were at low concentrations. The time of ozonation influenced the content of acid produced in chlorination process, positively for MCAA and negatively for DCAA.

#### Volatilization of HAAs during water boiling

The haloacetic acids have the boiling temperatures of about 200°C. It is well known that other disinfection by-products such as the trihalomethanes could be removed from drinking water by boiling what can improve the water quality.



Fig. 7. Content of THMs and HAAs in treated water.

Table 3.	Changes	of th	ne HAAs	during	water	boiling	
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HAA	Decrease of the acid (%)
MCAA	5-8
MBAA	26-31
DCAA	17–19
TCAA	69-72
DBAA	9–13

The possibility of removal the HAAs during water boiling was tested. A known amount of the HAAs was added to drinking water in Warsaw. Part of the water was stored for 24 h at a temperature *ca*.  $6^{\circ}$ C, the other part was boiled for 10 min; then the HAAs were determined. The concentration of HAA in cold water did not change. The losses of HAAs during boiling are presented in Table 3.

- the losses of MCAA were small (5-8%),
- the concentration of DBAA changed very little (9-13%),
- there was some removal of DCAA (17–19%),
- there was some loss of MBAA (26–31%),
- but the biggest losses were in case of TCAA (69–72%).

It can be explained by decomposition of TCAA in boiling.

$$CCl_3COOH \xrightarrow{boiling} CHCl_3 + CO_2$$

The volatile chloroform is produced, that belongs to the THMs group.

#### DISCUSSION

The concentration of haloacetic acids in water of Zegrzyńskie Lake was at the trace levels or below limits of detection. During the water ozonation very small amount of HAAs was produced.

The haloacetic acids were formed in the chlorination process. Mostly there were chlorinated compounds; at very low levels the brominated derivatives were produced.

Among the 5 HAAs the highest concentrations were found for DCAA and TCAA.

The concentrations of HAAs were changing with time and they were very dependent on the season. The lowest concentrations were determined in winter, when the water temperature was low, the biological production very small, (low concentration of algae) and low content of organic matter. The sum of HAAs was below 10  $\mu$ g/l.

The highest concentration of HAAs was noticed in the periods when the water temperature was high, the algae blooms occurred and the content of organic matter was the highest. The sum of the HAAs reached 120  $\mu$ g/l. The correlation between the content of HAAs and such parameters as COD, DOC, humic substances concentration and UV absorbance was noticed. The conclusion can be drawn that the HAAs formation was dependent on organic matter concentration (precursors).

But the much better correlation between the HAAs content and water temperature was found. There is the conclusion that the formation of HAAs depends greatly on water temperature.

The relationship between the HAAs content and doses of chlorine was also noticed.

A very close relationship between the content of HAAs and THMs was observed. The conclusion is that there was the same reason for HAAs and THMs formation.

The water ozonation and chlorination in laboratory conditions showed that the sum of HAAs was at the same level as that in the study of Warsaw Waterworks, but the proportion of individual HAA was different which can be caused by different conditions. It was found that time of ozonation can influence the formation of HAAs, some HAAs increase and other decreases with the longer time of ozonation. But the periods of ozonation in laboratory experiment were very long (up to 360 min), practically never used in water works.

The experiments were done on the removal of HAAs during water boiling like in the consumer's kitchen. The losses of four HAAs were rather small. The bigger removal of TCAA could be attributed to the decomposition of TCAA into chloroform.

There is the conclusion that water boiling does not easily removed the HAAs while it does is in case of THMs.

#### CONCLUSIONS

Water ozonation has small influence on the HAAs formation. The haloacetic acids are produced during water chlorination. The content of HAAs depended mostly on the water temperature and to a smaller extent on the concentration of organic matter. The water boiling does not remove the HAAs while it does in case of THMs.

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