

THE OCCURRENCE OF HALOACETIC ACIDS IN KRAKOW WATER
DISTRIBUTION SYSTEM

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Abstract: The article presents the results of the research on the water samples taken from the Krakow water distribution system and their pollution by haloacetic acids: monochloroacetic acid, monobromoacetic acid, dichloroacetic acid, trichloroacetic acid, bromochloroacetic acid and dibromoacetic acid. The water samples were taken from the extremities of the distribution systems (Raba and Bielany) in the city of Krakow. Both analyzed plants use the chlorination as the water treatment process, however, water for Raba and Bielany comes from different surface waters and differs in quality and organic matter concentration. These plants also apply different water treatment processes and their distribution systems have a different size. The objective of this study was to measure the haloacetic acids levels in these two water distribution systems, assess the correlation between the total trihalomethanes and the sum of six haloacetic acids, determine if trihalomethanes can be a good indicator to predict haloacetic acids concentration in water distribution systems.

INTRODUCTION

Chlorination is a cheap, efficient and easy way to disinfect water. It is widely used in the treatment of water. However, the use of chlorine may cause the formation of carcinogenic halo-organic compounds, as the disinfection by-products (DBPs), among which trihalomethanes (THMs) and haloacetic acids (HAAs), are the two major groups. THMs – trichloromethane (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM) and tribromomethane (TBM) are well tested and – due to the law regulations – routinely monitored in drinking water. HAAs include nine substances, but the most common are monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA) and bromochloroacetic acid (BCAA) [1, 14, 16]. Toxicology studies have shown that HAAs are potentially carcinogenic [14]. Dihaloacetic acids have the greatest health impacts, compared to mono- and trichloroacetic acids [11], mutagenicity of the brominated HAAs is higher than that of the chlorinated analogs [1]. Medical studies have shown that DCAA, DBAA, BCAA and TCAA are carcinogenic in laboratory tests on animals [1, 11]. DCAA has been classified as a probable human carcinogen – this compound can cause cancer,

reproductive and developmental effects. While TCAA has been classified as a possible human carcinogen, it can also cause detrimental effects on liver, kidney, spleen and also developmental effects [13].

Up to now, HAAs limit has not been defined in Polish drinking water regulations, but HAAs are regulated by WHO [17] and USEPA [15]. The WHO established a maximum contaminant limits for MCAA ($20 \mu\text{g}/\text{dm}^3$), DCAA ($50 \mu\text{g}/\text{dm}^3$) and TCAA ($200 \mu\text{g}/\text{dm}^3$). USEPA established limits for MCAA ($70 \mu\text{g}/\text{dm}^3$), TCAA ($20 \mu\text{g}/\text{dm}^3$) and HAA5 (the sum of five haloacetic acids: MCAA, DCAA, TCAA, MBAA, and DBAA) ($60 \mu\text{g}/\text{dm}^3$).

The level of DBPs varies according to the quality and quantity of natural organic matter (NOM) present in the treated water before disinfection [4, 6, 10]. To characterize NOM several researchers use the parameter SUVA_{254} (specific UV_{254} absorbance – UV absorbance divided by the DOC concentration). Higher values of SUVA indicate the higher potential of NOM to form DBPs [2, 3]. Other factors responsible for DBPs formation are a chlorine dose, pH of water, temperature, reaction time of chlorine with NOM (residence time of water in the distribution system). The formation of HAAs increases with an increase in temperature and decrease in pH [11, 14]. Longer reaction time causes the higher concentration of HAAs [11], however several researches observed a decrease of HAAs in finished drinking water despite extended reaction time [14].

The objective of this study was to measure the HAAs levels in two Krakow water distribution systems – Raba and Bielany, to assess the correlation between total THMs (TTHM) and a sum of six HAAs (HAA6) and to determine whether THMs are a good indicator to predict HAAs concentration in water distribution systems.

MATERIALS AND METHODS

Areas of study

Two water treatment plants and their distribution systems were an object of this study. The analyzed plants take water from different surface waters and apply different treatment processes. ‘Raba’ Water Treatment Plant (RWTP), which supplies the southern part of Krakow with potable water, takes water from the Dobczyce Reservoir. Water is treated with the following processes: ozonation, coagulation with aluminum sulphate, sand rapid filtration and chlorine disinfection. ‘Bielany’ Water Treatment Plant (BWTP), which supplies the western part of Krakow with potable water, takes water from the Sanka river. It is treated in the slow filter (infiltration) and chlorine disinfected. ‘Raba’ water distribution system (RWDS) is the biggest system in Krakow and supplies 55% of the city population with potable water. ‘Bielany’ water distribution system (BWDS) serves 10% of Krakow citizens.

Sampling procedure

The raw water samples were taken from a plant prior to the disinfection stage, but after all the other treatment processes, it was stored at 2 dm^3 bottles and kept at 4°C until the analysis (no longer than 24 h). Dissolved organic carbon (DOC), UV_{254} and pH were measured in these samples. After disinfection, the free chlorine concentration was measured in water directed to the distribution system.

Five tap water samples were taken from BWDS and six from RWDS to determine DBP (HAA and THM) concentration. These samples were collected avoiding bubble

formation and stored in 250 cm³ amber bottles with PTFE liners and kept at 4°C until analysis (no longer than 24 h). Sodium sulphite was used for quenching DBPs formation.

Analytical methods

The six HAAs were analyzed: MCAA, MBAA, DCAA, TCAA, BCAA and DBAA. HAA concentration was analyzed using acidic methanol esterification method [8, 9] and GC-MS (Trace Ultra DSQII, Thermo Scientific). Helium was used as the carrier gas. The RxiTM-5ms capillary column (Restek) was used (film thickness 0.5 µm; column length 30 m; column diameter 0.25 mm). The HAAs were extracted using the liquid-liquid extraction method with MTBE (methyl tert-butyl ether). 0.9 cm³ of the extract was transferred into a 15-cm³ amber vial, then 2 cm³ of a solution of sulphuric acid in methanol (10%) was added and the vial was placed in water bath at 50°C for 1 h. After this time the vial was cooled in 4°C for 10 min and 5 cm³ copper (II) sulphate pentahydrate and anhydrous sodium sulphate solution (50 g/dm³ and 100 g/dm³ respectively) was added. The vial was shaken for 2 min and allowed to stand for about 5 min. The upper layer was used for an injection into GC. The column was heated from 40°C (0 min) to 100°C (5 min) with the temperature increase rate of 40°C/min, then to 200°C (0 min) with the temperature increase rate of 8°C/min. The method detection limit was 0.5 µg/dm³ for MCAA and MBAA, 0.01 µg/dm³ for other HAAs.

The THM concentration was analyzed using a gas chromatograph with the Trace Ultra DSQII GC-MS mass spectrometer (Thermo Scientific). Helium was used as the carrier gas. The RxiTM-5ms capillary column (Restek) was used (film thickness 0.5 µm; column length 30 m; column diameter 0.25 mm). The THMs were extracted using the liquid-liquid extraction method with MTBE (methyl tert-butyl ether) and analyzed on the GS-MS. The column was heated from 35°C (9.5 min) to 200°C (0 min) with the temperature increase rate of 40°C/min. The method detection limit was 0.01 µg/dm³.

The DOC was analyzed following Polish Standard PN-EN 1484. To oxidize organic matter the chemical oxidation method in fluid phase was used (sodium persulphate/100°C) [5, 12]. CO₂ released in the process was analyzed using a gas chromatograph with the Trace Ultra DSQII GC-MS mass spectrometer (Thermo Scientific). The method detection limit was 0.3 mg/dm³.

The free chlorine was analyzed using the DPD (N,N-diethylphenylendiamine) method (according to Polish Standard PN-ISO 7393-2). The free chlorine concentration was measured using the Aurius 2021 UV-VIS spectrophotometer (Cecil Instruments). The detection limit was 0.03 mg/dm³ for this method.

UV₂₅₄ absorbance was measured by the Aurius 2021 UV-VIS spectrophotometer (Cecil Instruments).

RESULTS AND DISCUSSION

Characteristic of raw water

Table 1 presents the characteristic of the water samples from a plant prior to the disinfection stage, but following all the other treatment processes.

Table 1. Quality of treated water (before chlorinated) from Bielany and Raba Treatment Plants

	DOC (mg/dm ³)	UV254 (cm ⁻¹)	SUVA (cm ⁻¹ ·dm ³ /mg)	pH
Bielany Water Treatment Plant	5.3	0.073	0.014	7.48
Raba Water Treatment Plant	3.3	0.027	0.008	7.88

The water from RWTP had the lower organic matter content (DOC = 3.3 mg/dm³) than water from BWTP (DOC = 5.3 mg/dm³). Also the SUVA parameter for water from RWTP (SUVA = 0.008 cm⁻¹·dm³/mg) was lower than for water from BWTP (SUVA = 0.014 cm⁻¹·dm³/mg). Free chlorine concentration in water after disinfection from BWTP was 0.37 mg/dm³, while in water from RWTP it was 0.43 mg/dm³. Due to the length of the distribution system, water from RWTP is additionally chlorinated in the pipeline. pH of water from RWTP was higher than pH of water from BWTP, and it was respectively 7.77 and 7.48.

HAAs in finished drinking water

Table 2 presents the concentration of HAAs and THMs in finished drinking water samples taken from the BWDS and RWDS.

Table 2. The concentration of HAAs and THMs from Bielany and Raba distribution system

	Concentration of disinfection-by products (µg/dm ³)									
	MCAA	MBAA	DCAA	TCAA	BCAA	DBAA	TCM	BDCM	DBCM	TBM
Bielany water distribution system										
B1	2.95	1.35	4.00	3.77	0.55	0.37	7.83	2.22	2.29	0.01
B2	1.41	3.09	3.00	3.23	0.88	0.30	5.86	2.15	1.41	0.06
B3	n.d.	2.08	3.17	2.28	0.40	0.26	7.76	1.95	1.93	0.03
B4	0.58	0.50	3.35	1.52	0.84	0.04	5.96	4.38	1.83	0.05
B5	n.d.	0.89	3.38	2.51	0.22	0.24	5.55	2.85	1.26	0.08
Raba water distribution system										
R1	1.64	1.46	2.67	3.18	0.30	0.03	6.81	1.51	0.57	0.03
R2	n.d.	1.31	1.78	2.84	0.26	0.17	10.09	1.87	0.40	n.d.
R3	2.64	0.87	2.85	2.08	0.32	n.d.	11.10	2.79	0.39	0.08
R4	2.48	0.83	2.35	3.24	0.12	0.10	9.54	2.71	0.76	0.01
R5	n.d.	1.18	2.71	4.06	0.12	0.10	12.50	2.63	0.75	0.02
R6	6.63	1.05	3.12	4.00	0.50	0.16	12.19	3.27	0.81	0.17

n.d. – not detected

Figure 1 presents the minimum, maximum and average values of particular HAAs and HAA6.

Although treated water (before disinfection) in BWTP had higher SUVA and DOC concentration, HAAs levels in the RWDS were significantly higher than in BWDS. The water samples from RWDS contained on average between 6.36 µg/dm³ and 15.46 µg/dm³ HAA6, while water from BWDS between 6.82 µg/dm³ and 12.99 µg/dm³. Because

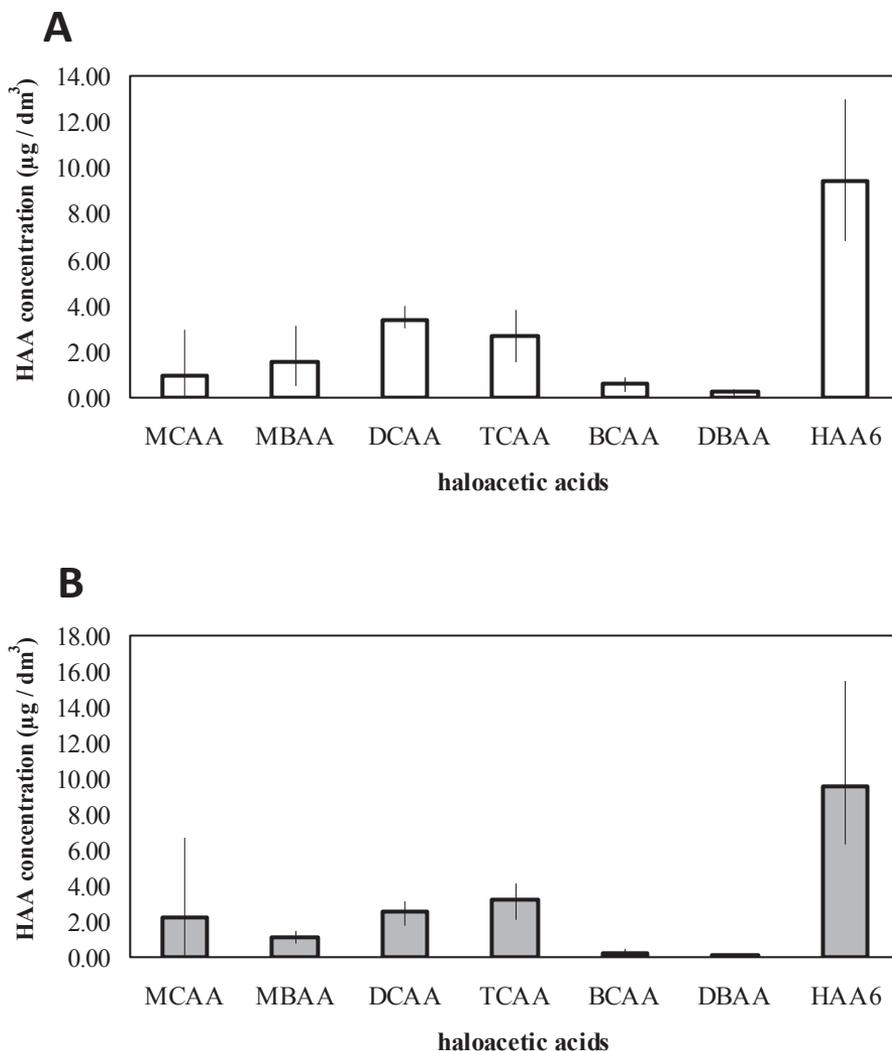


Figure 1. Occurrence of HAAs in water distribution systems in Krakow
(A) Bielany (B) Raba

of the long distribution system, water from RWDS is additionally chlorinated and this additional chlorine dose can be a reason of the higher amount of HAAs, despite the better parameters of original water. In both BWDS and RWDS the concentrations of individual HAAs and their sum were low and did not exceed the maximum contaminant limits regulated by WHO [17] and USEPA [15].

As can be observed in Figure 2, DCAA and TCAA were two major species of HAAs found in waters from BWDS and RWDS.

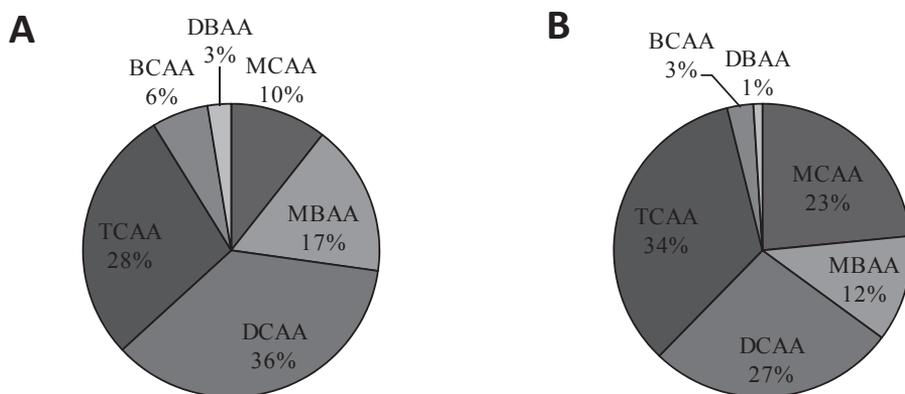


Figure 2. HAAs species in water distribution systems in Krakow
(A) Bielany (B) Raba

The sum of these two species represents more than 60% of all HAAs in both analyzed distribution systems. DCAA and TCAA are the most important among HAAs due to their high health impact. DBAA and BCAA acids constituted the smallest group. DBAA concentration was 3% in water taken from BWDS and 1% from RWDS, for BCAA it was 6% and 3% respectively. Percentage concentration of monohaloacetic acids was: 10% for MCAA and 17% for MBAA for BWDS, and respectively for RWDS – 23% and 12%.

Relationships between HAAs and THMs

Figure 3 presents relationships between HAA6 and TTHM for all samples from two distribution systems, and also for each distribution system separately.

As shown in Figure 3A there are good correlations ($R^2 = 0.9758$) between HAAs and THMs for samples from both studied water distribution systems together, despite the differences in the treatment process, quality of raw waters, chlorine dose and length of distribution systems. When analyzing the correlations between HAAs and THMs for each distribution system separately, a linear correlation was $R^2 = 0.9933$ for BWDS (Figure 3B) and $R^2 = 0.9736$ for RWDS (Figure 3C). It means, that basing on the THM concentrations, which are regularly and obligatorily measured, the HAA concentrations in distribution systems can be predicted with the high probability. The other authors' studies proved the good correlation between THMs and HAAs [14, 16], however due to the research of Malliarou *et. al.* [7] in some cases such correlation was not observed.

CONCLUSIONS

The studies conducted on samples from two water distribution systems supplying the city of Krakow with potable water (Raba and Bielany) have shown the following:

- HAA concentration in water samples taken from Krakow water distribution systems was low (max 12.99 $\mu\text{g}/\text{dm}^3$ for Bielany and 15.46 $\mu\text{g}/\text{dm}^3$ for Raba) and did not exceed the maximum contaminant limits regulated by WHO [17] and USEPA [15];
- DCAA and TCAA were the two major species of HAAs found in water samples from BWDS and RWDS – the sum of these two species represents more than 60%

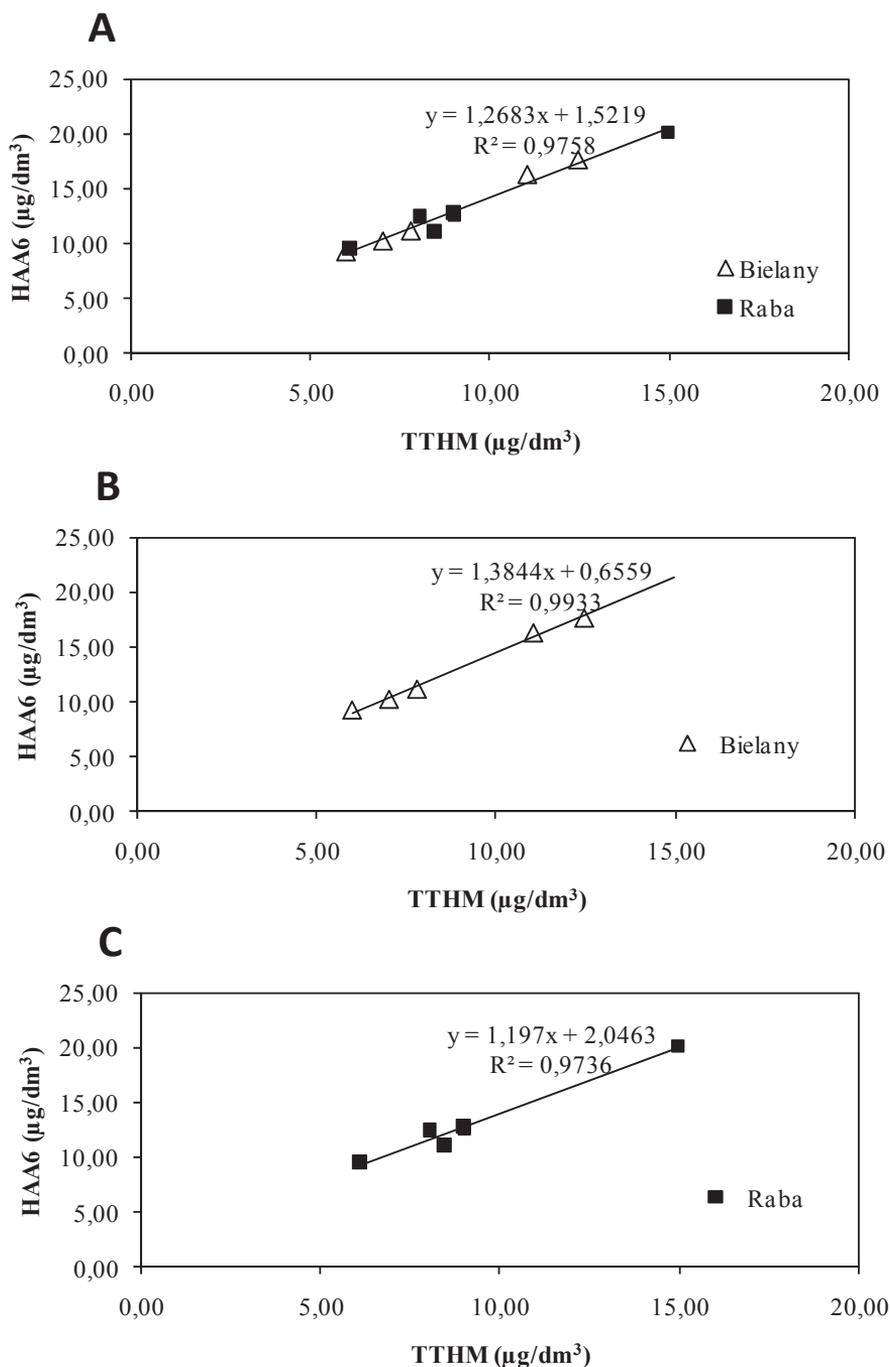


Figure 3. Relationships between HAA6 and TTHMs (A) all data for the two distribution systems (B) data for 'Bielany' distribution system (C) data for 'Raba' distribution system

- of HAAs in each examined distribution system;
- HAAs and THMs have a high linear correlation ($R^2 > 0.97$) for each distribution system and the levels of HAAs may be estimated from THM concentration.

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WYSTĘPOWANIE KWAŚÓW HALOGENOOCTOWYCH W KRAKOWSKIM SYSTEMIE DYSTRYBUCCJI WODY

W artykule przedstawiono wyniki badań wody pochodzącej z krakowskich wodociągów, na zawartość kwasów halogenooctowych – kwasu monochlorooctowego, kwasu monobromooctowego, kwasu dichlorooctowego, kwasu trichlorooctowego, kwasu bromochlorooctowego i kwasu dibromooctowego. Wodę pobierano w końcówkach sieci systemów dystrybucji wody pitnej miasta Krakowa, zaopatrywanych z Zakładu Uzdantnia Wody (ZUW) Raba i ZUW Bielany. Obydwa rozpatrywane Zakłady Uzdantniania Wody stosują chlorowanie

jako proces uzdatniania wody pitnej. Woda ZUW Raba i ZUW Bielany różni się zarówno jakością, jak i ilością materii organicznej, ponieważ pochodzi z różnych źródeł wody powierzchniowej. Zakłady te różnią się również procesem uzdatniania wody pitnej, a także wielkością sieci dystrybucji wody. Celem przedstawionych badań był pomiar stężeń kwasów halogenooctowych w systemach dystrybucji wody zasilanych przez ZUW Raba i ZUW Bielany, określenie korelacji pomiędzy sumą trihalometanów i sumą sześciu kwasów halogenooctowych, ustalenie czy zawartość trihalometanów może służyć jako indykator do przewidywania stężeń kwasów halogenooctowych w systemach dystrybucji wody.