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Occurrence of volatile organic chlorination by-products in water distribution system in Krakow (Poland)

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ABSTRACT

The goal of this paper is to analyze the Krakow water distribution systems regarding the occurrence of volatile halogenated water disinfection by-products from the group of trihalomethanes (trichloromethane, bromodichloromethane, dibromochloromethane, and tribromomethane), haloacetonitriles (bromochloroacetonitrile, dibromoacetonitrile, dichloroacetonitrile, and trichloroacetonitrile), haloketones (1,1-dichloro-2-propanone and 1,1,1-trichloro-2-propanone), chloropicrin (trichloronitromethane), and chloral hydrate. The research was conducted since February 2011 to March 2012; water samples were taken from the ends of the pipe system and analyzed. Two water distribution systems were selected for the research: the first one supplied with water from the water treatment plant (WTP) Raba, and second one—from WTP Bielany. These systems differ in water quality, applied water treatment processes, and the size of the water distribution system, however, in both plants chlorination is applied for the disinfection process. Each month, five samples were taken from the distribution system of WTP Bielany, and six samples from WTP Raba for research. During the entire research period, totally, 154 samples were taken (84 from WTP Raba distribution system and 70 from WTP Bielany one), in which 12 by-products were analyzed. The results of this analysis were used to assess the occurrence of volatile water disinfection by-products in the considered water distribution systems.

Keywords: Disinfection by-products; Trihalomethanes; Haloacetonitriles; Haloketones; Chloral hydrate; Chloropicrin; Distribution systems

1. Introduction

The application of chemical disinfectants (including chlorine) during water treatment is frequently necessary in order to eliminate secondary water contamination. Using chemical compounds is integrally connected with their reactivity and forming of halogenated disinfection by-products (DBPs). The main DBPs in drinking water includes: trihalomethanes (THM), haloacetic acids (HAA), haloacetonitriles (HAN), haloketones (HK), chloral hydrate (CH), and halonitromethanes (HNM) [1,2]. These compounds are

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of scientific interest, due to the risk for human health. Most research activities focus on THM—the biggest group of by-products, which are monitored on daily basis in numerous countries in the world. Also, there are several studies on HAA—the DBPs group, which is the second one, taking into consideration, the amount of formed compounds. There are relatively few publications on HK or N-DBPs (DBPs containing nitrogen), such as HAN and HNM [3–7], while the nitrogen derivatives are far more toxic than the disinfection by-products whose structure is based on the atom of carbon [8]. Generally, N-DBPs concentration is low in water, as well as is brominated DBPs (Br-DBPs) one. However, when bromide is present in chlorinated water, the levels of Br-DBPs can be higher than chlorinated DBPs [9]. Bromine easily reacts with organic compounds. Thus, the concentration of bromide in water causes the generation of Br-DBPs and by-products which are bromine and chlorine derivatives [10]. It also limits the formation of chlorinated by-products [11]. Due to the presence of bromide in water, Br-DBPs are generated instead of THM [12]. In the case of dihaloacetonitriles—bromochloroacetonitrile (BCAN) and dibromoacetonitrile (DBAN) are generated instead of dichloroacetonitrile (DCAN) [13]. Since Br-DBPs are more dangerous for human health than their chlorinated equivalents [8], the bromine incorporation factor (BIF) [14,15] has been created to assess Br-DBPs share in the particular group of DBPs. The equation to calculate BIF for THM is given below; the molar concentration of individual THM should be used in it.

$$\mathrm{BIF(THM)} = \frac{0 \cdot [\mathrm{TCM}] + 1 \cdot [\mathrm{BDCM}] + 2 \cdot [\mathrm{DBCM}] + 3 \cdot [\mathrm{TBM}]}{3([\mathrm{TCM}] + [\mathrm{BDCM}] + [\mathrm{DBCM}] + [\mathrm{TBM}])}$$

For other DBPs this factor is calculated analogously. The values of BIF factor are in the range from 0 to 1. In the case of THM—BIF equals to 0, which means that there is only TCM present in water (no brominated derivatives), while BIF is 1, which means TBM is the only generated compound [14].

Besides bromide presence in chlorinated water, DBPs concentration in water distribution systems depends on several parameters of water such as pH, the concentration, and characteristics of natural organic matter, a dose of chlorine, the temperature of distributed water, and the size of network being directly connected with the reaction time of chlorine with the DBPs precursors [16–25].

DBPs are categorized into bigger groups, based on their physical or chemical characteristics. Halogenated chlorination by-products (CBPs) are mostly divided on non-volatile chlorination by-products, to which HAA are classified, and volatile chlorination by-products (VCBPs), to which the following by-products are classified: THM, HAN, HK, CH, and HNM including chloropicrin (CP) [26,27].

Humans can be exposed to the impact of DBPs not only as a result of disinfected water consumption, but also by inhalation and skin contact during regular domestic activities such as bathing, taking shower, washing, and cooking [16]. Inhalation and skin contact associated with bathing are responsible for 30–50% of the total cancer risk connected with DBPs. Due to their physical characteristics, VCBPs easily transform into gas form, thus inhalation risk is particularly high, especially during hot tubs, when the water temperature is 35–45˚C [16].

In the paper, there are presented research results on the occurrence of VCBPs in water from ends of Krakow water distribution systems. In the water samples taken during the period of 14 months, the following parameters were analyzed:

- THM—trichloromethane (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM), and tribromomethane (TBM);
- HAN—trichloroacetonitrile (TCA), DCA, BCA, and DBA;
- HK—1,1-dichloroproponone (1,1-DCP) and 1,1,1-trichloropropanone (1,1,1-TCP);
- CH and CP.

2. Materials and methods

2.1. Study area and sampling points

The research was conducted on Krakow water from distribution systems supplied by water treatment plant (WTP) Raba and WTP Bielany. Both analyzed plants apply chlorination to disinfect water, but take water from different sources and apply different treatment processes. WTP Raba supplies the southern part of Krakow with potable water. Water is taken from the Dobczyce Reservoir and it undergoes such processes as ozonation, coagulation with polyaluminum chlorides, sand rapid filtration, and chlorine disinfection. Due to a big size of the distribution system supplied by WTP Raba, water is additionally chlorinated. WTP Bielany supplies the western part of Krakow. Water is taken from the Sanka River, treated in the sedimentation and slow filtration processes, and disinfected with chlorine.

Water samples were selected for research from five points in the supply zone of ZUW Bielany (B1–B5) and six points from ZUW Raba (R1–R6). The water network in the city of Krakow is the connected system in which water can origin from different WTPs depending on its consumption. To avoid taking water mixed from different WTPs, the selection of sampling points was consulted with the Central Laboratory of Municipal Waterworks and Sewer Enterprise in Krakow. The distance from the WTPs was taken into the consideration when selecting the points. The ones located in the vicinity of the main pipelines were selected. The localization of water sampling points is presented in Fig. 1.

2.2. Water sample collection

Water samples were taken during a period of 14 months, namely, since February 2011 to March 2012. From the distribution system of WTP Bielany, five samples were taken each month of the research, and from WTP Raba—six ones were taken. Throughout the entire research period, 154 samples were taken (84 from WTP Raba distribution system and 70 from WTP Bielany one), in which 12 by-products were analyzed. Additionally, each month, water was taken directly from both WTPs and analyzed to determine the quality of water prior chlorination. Thus, samples were taken from water after all treatment processes, but before chlorination. The samples from WTPs were taken into bottles of volume 2 dm^3 and stored in the temperature 4°C (not longer than 24 h). In these samples, the following parameters were measured: dissolved organic carbon (DOC), UV absorbance in 254 nm (UV_{254}), bromide concentration, nitrogen compounds concentration, and pH. During each sampling, chlorine doses (Cl_2) were also recorded (in the case of Raba system they are the sums of chlorine doses from both WTP and additional chlorination realized during water transport).

Samples from water network ends were taken into dark-glass bottles of volume 250 cm^3, with the silicon sealing covered with PTFE. Before filling the bottles, water flow had been open for several minutes, until water temperature stabilized. The bottles were completely filled to avoid air bubbles. This filling process was conducted gently and carefully in order not to flush out dechlorator (ascorbic acid). The water temperature and pH were measured on-site. Directly after taking the samples, they were transported to the laboratory of the Department of Environmental Management and Protection, where they were soon extracted in order to analyze volatile chlorination DBPs. The samples were not stored.

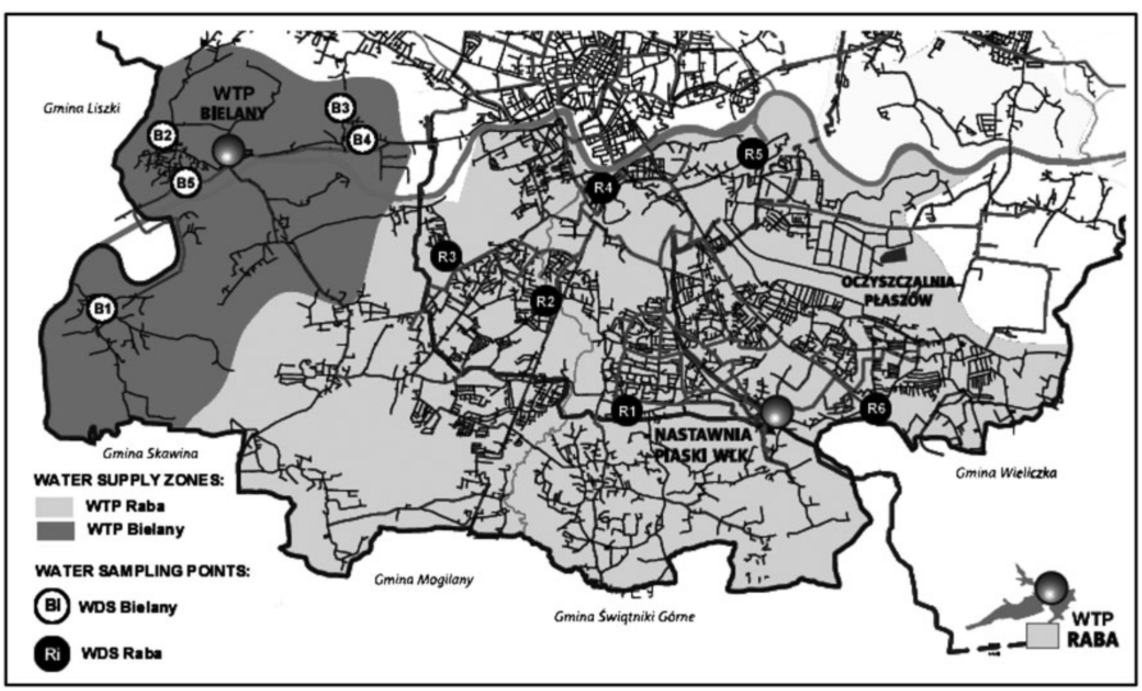

Fig. 1. The localization of points, in which water samples were taken from networks supplied by WTP Raba and WTP Bielany (based on [28]).

2.3. Analytical methods

The VCBPs concentrations were analyzed using a gas chromatograph with a Trace Ultra DSQII GC–MS mass spectrometer (Thermo Scientific). Helium was used as the carrier gas. The Rxi™-5 ms capillary column (Restek) was used (film thickness 0.5 µm, column length 30 m, column diameter 0.25 mm). The THM, HAN, HK, CH and CP were extracted using a liquid–liquid extraction method with MTBE (methyl tert-butyl ether) and analyzed on the GS–MS. The column was heated from 35℃ (9.5 min) to 200℃ (0 min) with the temperature increase rate of 40℃/min. The method detection limit was 0.01 µg/dm^3.

DOC was analyzed in accordance with Polish Standard PN-EN 1484. To oxidize organic matter, the method of the chemical oxidation in fluid phase was applied (sodium persulfate/100℃). CO_2 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 0.03 mg/dm^3.

The nitrogen compounds were analyzed using Nanocolor tests. Dissolved organic nitrogen (DON) concentration was calculated as a difference of total nitrogen (TN) and inorganic nitrogen (NH_4-N, NO_2-N, and NO_3-N). Nitrogen compounds were analyzed in photometric cuvettes (5-cm length) and with the Aurius 2021 UV–vis spectrophotometer (Cecil Instruments). The detection limits for the nitrogen compounds were as follows: TN—0.1 mg/dm^3; NH_4-N—0.01 mg/dm^3; NO_2-N—0.002 mg/dm^3; and NO_3-N—0.02 mg/dm^3.

The bromide ion concentration was determined with the use of a spectrophotometric method using oxidation of Br^- with chloramines-T and the subsequent bromination of phenol red. It was measured using the Aurius 2021 UV–vis spectrophotometer (Cecil Instruments). The detection limit of this method was 0.1 mg/dm^3.

3. Results and discussion

3.1. Quality of water prior chlorination

The results of water quality analysis from WTP Raba and WTP Bielany after all treatment processes, but before chlorination, are presented in Table 1.

The water samples from the WTP Raba had lower values of DOC in comparison with the ones from WTP Bielany (mean concentration of DOC was 2.1 and 3.2 mg/dm^3, respectively). To assess the quality of organic matter, besides TOC, the specific ultraviolet absorbance ($SUVA_{254}$) was determined in each water sample. $SUVA_{254}$ is the UV absorbance divided by the DOC concentration. Water samples contain the hydrophobic, aromatic, and high molecular weight fractions of NOM (such as humic and fulvic acids) have higher UV_{254} and higher $SUVA_{254}$, while the hydrophilic fractions of NOM cause lower UV_{254} and lower $SUVA_{254}$. The analyzed water samples from WTP Bielany had higher values of $SUVA_{254}$ (8.327 dm^3 mg^{-1} m^{-1}) rather than water from WTP Raba (5.229 dm^3 mg^{-1} m^{-1}). The samples from WTP Bielany had also higher level of organic nitrogen, the average DON concentration was 0.18 mg/dm^3 for water from WTP Bielany, and 0.11 mg/dm^3 for samples from WTP Raba. As it can be observed in Table 1, the samples from WTP Bielany had the higher average bromide concentration (0.6 mg/dm^3) than those from WTP Raba (0.3 mg/dm^3).

3.2. Concentration of individual groups of VCBPs

In Table 2, statistical data on concentrations of individual VCBPs have been presented, as well as pH and temperature in water distribution systems supplied by WTP Raba and WTP Bielany.

During the research period, more VCBPs were formed altogether in WTP Raba distribution system in comparison with the Bielany one. The mean and median of total VCBPs for WTP Raba system were 56.80 and 51.74 µg/dm^3, respectively, while for WTP Bielany—48.62 µg/dm^3 and 44.39 µg/dm^3. The highest concentration of total VCBPs (136.88 µg/dm^3) was observed for WTP Raba distribution system in September 2011, while for WTP Bielany network it was 103.50 µg/dm^3, which was observed in August 2011. The minimum value of the total VCBPs was 19.65 µg/dm^3 for Raba distribution system (March 2011) and 10.50 µg/dm^3 for Bielany one (June 2011).

In both water distribution systems of WTP Bielany and WTP Raba, the dominant compound was TCM. Its average concentration during 14-month-experiments was 15.81 µg/dm^3 for WTP Raba and 7.04 µg/dm^3 for WTP Bielany. Its median, maximum, and minimum values for WPT Raba were, respectively, 12.15, 47.64, and 4.11 µg/dm^3, and for WTP Bielany—5.65, 24.93, and 0.78 µg/dm^3. Polish legislation defines the standard for TCM in potable water to be at the level of 30 µg/dm^3. In Raba distribution system, this value was exceeded in several cases: in July 2011 in points R3, R4, R5, and R6; in August 2011 in R1, R2, R4, and R6; in September 2011 in R2, R4, and R6. The highest level of TCM was observed in August 2011 in the point R6 (47.64 µg/dm^3). In remaining months of observations, TCM concentration was much lower than the normal one.

Table 1
Quality of water prior chlorination and chlorine doses in WTP Raba and WTP Bielany

		Concentration levels			
Parameter	No. of samples	Mean	Min.	Max.	Median
WTP Raba					
DOC, mg/dm^3	14	2.1	1.1	3.7	1.7
UV_{254}, cm^{-1}	14	0.096	0.048	0.135	0.105
$SUVA_{254}$, $dm^3 mg^{-1} m^{-1}$	14	5.229	1.814	9.595	4.710
Br^-, mg/dm^3	14	0.3	0.2	0.4	0.3
DON, mg/dm^3	14	0.11	0.02	0.31	0.07
NO_3-N, mg/dm^3	14	1.10	0.58	1.78	1.15
NO_2-N, mg/dm^3	14	0.003	nd	0.012	nd
NH_4-N, mg/dm^3	14	0.02	nd	0.06	0.01
Cl_2, mg/dm^3	14	0.8	0.7	1.1	0.8
WTP Bielany					
DOC, mg/dm^3	14	3.2	1.5	6.0	3.1
UV_{254}, cm^{-1}	14	0.245	0.180	0.365	0.224
$SUVA_{254}$, $dm^3 mg^{-1} m^{-1}$	14	8.327	4.941	15.234	7.829
Br^-, mg/dm^3	14	0.6	0.4	0.8	0.6
DON, mg/dm^3	14	0.18	0.02	0.53	0.11
NO_3-N, mg/dm^3	14	3.00	2.29	3.66	2.95
NO_2-Nv	14	nd	nd	0.005	nd
NH_4-N, mg/dm^3	14	0.03	nd	0.10	0.02
Cl_{2v}	14	1.8	1.6	2.3	1.7

nd—not detected.

BDCM was another compound taken into consideration while observing the concentrations in both distribution systems. The mean and median of its concentration for the entire period of experiment were, respectively, 3.65 and 3.35 $\mu g/dm^3$ for WTP Raba distribution system, and 5.53 $\mu g/dm^3$ and 5.36 $\mu g/dm^3$ for WTP Bielany. The maximum observed value was 8.56 $\mu g/dm^3$ for WTP Raba and 13.40 $\mu g/dm^3$ for WTP Bielany, and minimum—1.19 $\mu g/dm^3$ and 0.94 $\mu g/dm^3$, respectively. Polish legislation defines the standard for BDCM in potable water to be at the level of 15 $\mu g/dm^3$. This value was never exceeded during the research period in WTP Raba distribution system nor in WTP Bielany one. However, higher BDCM concentrations were observed for WTP Bielany rather than for WTP Raba. This could be due to relatively higher concentrations of bromide in water from WTP Bielany (see Table 1).

The third compound, taking into account the amount formed in water from WTP Raba distribution system, was CH with its average concentration 2.71 $\mu g/dm^3$ and median 2.53 $\mu g/dm^3$. Its maximum and minimum concentrations measured for WTP Raba network were 6.74 and 0.34 $\mu g/dm^3$. Water ozonation prior its chlorination promotes CH formation. In research of Koudjonou [29], the ratio of CH/∑THM in ozoned water (before chlorination) was from 12 to 52%, while for chlorinated water CH formation potential is low (4–22%). For water from WTP Raba, where ozonation is applied as the first stage of water treatment, the average CH/∑THM ration was 18%. For WTP Bielany water distribution system, CH was fourth compound regarding the formed amount, and the CH/∑THM ratio was 12%. Thus it was lower than for WTP Raba. The subsequent compounds formed in the water distribution system of WTP Raba were: 1,1,1-TCP; 1,1-DCP; DBCM; DCAN; BCAN; DBAN; TBM and CP. In water distribution system supplied by WTP Bielany, besides TCM and BDCM, the following compounds were formed: DBCM; CH; 1,1,1-TCP; 1,1-DCP; TBM; DCAN; DBAN; BCAN; CP; and TCAN.

Apart from the impact of water ozonation on CH formation mentioned above, there are several factors potentially causing the ratio of DBPs in water from analyzed water distribution systems. For instance, in water from WTP Bielany, compared to WTP Raba, the higher concentration of bromides and organic nitrogen were observed, which resulted in the relatively higher Br-DBPs and N-DBPs formation in water distribution

Table 2
Quality of water in distribution systems supplied by WTP Raba and WTP Bielany

Parameter	No. of samples	Concentration levels			
		Mean	Min.	Max.	Median
WTP Raba					
TCM, μg/dm^3	84	15.81	4.11	47.64	12.15
BDCM, μg/dm^3	84	3.65	1.19	8.56	3.35
DBCM, μg/dm^3	84	1.3	0.33	4.76	0.97
TBM, μg/dm^3	84	0.23	nd	2.52	0.05
∑THM, μg/dm^3	84	21.0	6.53	55.23	17.26
TCAN, μg/dm^3	84	0.13	nd	1.13	0.05
DCAN, μg/dm^3	84	1.09	0.14	8.34	0.80
BCAN, μg/dm^3	84	0.68	nd	5.14	0.33
DBAN, μg/dm^3	84	0.39	nd	3.87	0.12
∑HAN, μg/dm^3	84	2.29	0.40	8.86	1.46
1,1-DCP, μg/dm^3	84	1.78	nd	9.21	1.26
1,1,1-TCP, μg/dm^3	84	1.94	nd	7.09	1.55
∑HK, μg/dm^3	84	3.72	nd	13.88	2.82
CH, μg/dm^3	84	2.71	0.34	6.74	2.53
CP, μg/dm^3	84	0.08	nd	0.43	0.04
pH	84	7.97	7.60	8.23	8.00
T, ℃	84	13.5	0.5	22.0	15.0
WTP Bielany					
TCM, μg/dm^3	70	7.04	0.78	24.93	5.65
BDCM, μg/dm^3	70	5.53	0.94	13.40	5.36
DBCM, μg/dm^3	70	4.08	nd	12.90	3.40
TBM, μg/dm^3	70	1.00	nd	6.61	0.46
∑THM, μg/dm^3	70	17.64	3.54	36.73	15.60
TCAN, μg/dm^3	70	0.10	nd	1.32	0.04
DCAN, μg/dm^3	70	0.91	nd	5.36	0.50
BCAN, μg/dm^3	70	0.64	nd	7.38	0.23
DBAN, μg/dm^3	70	0.75	nd	9.56	0.10
∑HAN, μg/dm^3	70	2.40	nd	13.05	1.10
1,1-DCP, μg/dm^3	70	1.42	nd	5.71	1.15
1,1,1-TCP, μg/dm^3	70	1.76	nd	7.46	1.11
∑HK, μg/dm^3	70	3.18	nd	9.21	2.61
CH, μg/dm^3	70	2.08	nd	8.55	1.23
CP, μg/dm^3	70	0.10	nd	0.54	0.06
pH	70	7.56	7.40	7.79	7.57
T, ℃	70	13.0	0.5	24.0	14.5

nd—not detected.

system. The bromide concentration in water causes the generation of Br-DBPs and by-products which are bromine and chlorine derivatives [10], it also limits the formation of chlorinated by-products [11]. DBPs formation could also be controlled by pH. The higher values of pH promote the formation of by-products from THM group, but in the case of HAN, as well as HK, a decrease in their concentration is observed with pH increase. This phenomena can be explained by the fact that these compounds are hydrolyzed and decomposed in the presence of chlorine in alkaline conditions and become intermediate products which form TCM. On the other hand, analyzing their formation in time, both for HAN and HK, independently from pH, after their initial formation, they gradually disappear in water. Thus, longer water distribution pipelines cause a decrease in HAN and HK formation [10,11]. According to other research reports [30], higher CH concentrations were observed in water with higher values of pH. According to literature with regard to that issue, the ozonation before chlorination can enhance CP formation [13], but in the case of Raba system, the average CP concentration was lower than in Bielany. It indicates a strong influence of chlorinated water quality (especially organic nitrogen content) on dynamics of CP formation in distribution system. According to literary sources, the influence of pH on CP formation is ambiguous. Mitch et al. [6], analyzing CP content for 72 h reaction time and pH values: 5, 7, and 9, observed higher CP concentration in the sample with pH 9 and the lowest one with pH 7. Shan et al. [5], studying compounds containing nitrogen showed that the alkaline conditions promotes HNM formation in ozonated and chlorinated water, however, this effect strongly differed for different precursors. In water which was only chlorinated, the pH influence on HNM was not observed.

The compounds from the THM group had the biggest share in analyzed DBPs for both concerned water distribution systems. The average value of total THM for WTP Raba system was 21.00 μg/dm^3, while for WTP Bielany—17,64 μg/dm^3 (median was 17.26 and 15.60 μg/dm^3, respectively). The maximum and minimum values of the sum of THM were 55.23 and 6.53 μg/dm^3 for WTP Raba, 36.73 and 3.54 μg/dm^3 for WTP Bielany. The percentage share of individual groups of compounds in the total VCBPs formed in the water distribution system is presented in Fig. 2 (A) for WTP Raba and in Fig. 2 (B) for WTP Bielany. THM constituted 70.5% of all analyzed VCBPs in the distribution system supplied by WTP Raba, and the slightly lower value—69.4% in a case of WTP Bielany.

HK were the second biggest group of formed VCBPs in both water distribution systems. Their percentage share, both for WTP Raba distribution system and WTP Bielany, was 12.5%. Regarding the concentration in WTP Raba distribution system, the following compounds should be listed: CH (9.0%), HAN (7.7%), and CP (0.3%). For WTP Bielany system, due to higher concentration of organic nitrogen, HAN share was higher—9.5%, CH—8.2%, while CP similarly to WTP Raba was formed in the lowest amount and constituted only 0.4% of all analyzed VCBPs.

The concentration of the sum of TCAN, DCAN, BCAN, and DBAN was in a range from 0.40 μg/dm^3 to 8.86 μg/dm^3 in WTP Raba distribution system, and from not detected to 13.05 μg/dm^3 in WTP Bielany one. The average concentration of all HAN was 2.29 μg/dm^3 for WTP Raba (median 1.46 μg/dm^3) and 2.40 μg/dm^3 for WTP Bielany (median 1.10 μg/dm^3). Both observed concentrations and the percentage share of individual groups of VCBPs were similar to those reported in the references and literature [9, 31, 32].

3.3. Distribution of individual compounds in groups of VCBPs

The distribution of individual compounds in THM group is presented in Fig. 3, both for the water distribution system supplied by WTP Raba (Fig. 3(A)) and the one by WTP Bielany (Fig. 3(B)).

TCM was a compound which was generated in the highest amount in both systems, however, due to higher concentration of bromide in water from WTP Bielany (Table 1), in the distribution system supplied by this plant, a higher share of brominated THM was observed in comparison with WTP Raba system. Bromide derivatives are generated instead of their chlorine equivalents [11], and this is the reason why TCM concentration in WTP Bielany network was lower. The influence of bromide on THM formation was so significant, that in some months (November 2011 to March

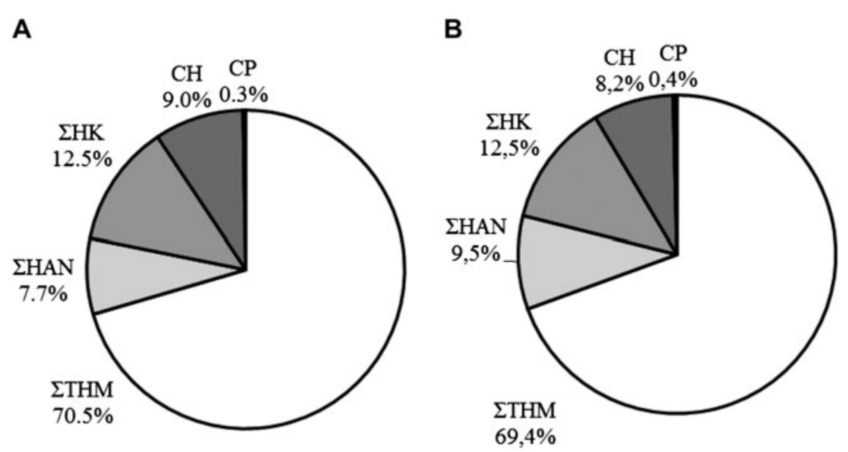

Fig. 2. The distribution of VCBPs groups in water distribution systems: (A) WTP Raba and (B) WTP Bielany.

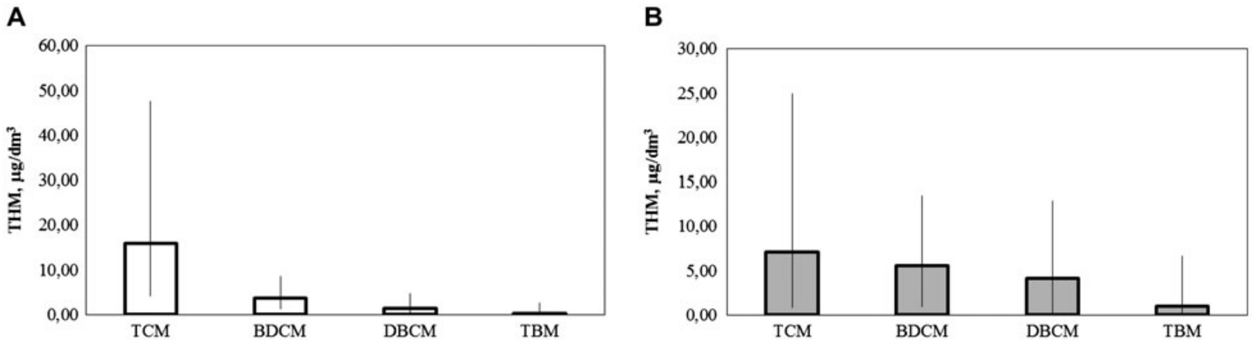

Fig. 3. The concentration of individual compounds in THM group in the water distribution system of: (A) WTP Raba and (B) WTP Bielany.

2012) BDCM concentration was higher than TCM concentration. The average share of TCM in a group of THM in WTP Raba distribution system was 75%, BDCM—18%, DBCM—6%, and TBM—1%. In WTP Bielany network, the distribution of these compounds was slightly different—TCM constituted 40% of all THM, BDCM, and DBCM—respectively, 31% and 23%, TBM share was the lowest—6%. Such distribution of individual brominated THM is rather specific since usually the share of these compounds is similar to one observed in WTP Raba system. The BIF ratio [14], [15] calculated for WTP Raba distribution system, using the average values of individual THM concentration, was 0.08, while for WTP Bielany network it was as high as 0.24. It is an indicator of a higher molar share of brominated THM in WTP Bielany distribution system when compared with WTP Raba.

The distribution of HAN is presented in Fig. 4, both for the water distribution system supplied by WTP Raba (Fig. 4(A)) and the one by WTP Bielany (Fig. 4(B)). As it can be observed in Fig. 4, the highest share in both systems had DCAN (48% for WTP Raba and 38% for WTP Bielany), while TCAN had the lowest one (5% and 4%, respectively). Similar HAN distributions are frequently reported in the literature [31]. BCAN share among all HAN was 30% for WTP Raba network, and 27% for WTP Bielany. Similarly, in the case of THM, the higher share of brominated HAN was observed in water from WTP Bielany. DBAN was 17% of all HAN in WTP Raba network, and 31% in WTP Bielany. The BIF ratio for this group of compounds did not differ significantly between the values for WTP Raba network (0.24) and WTP Bielany one (0.35), however, the share of brominated HAN was higher for water from WTP Bielany. HAN precursors react more easily with bromine and chlorine rather than precursors of other DBPs. [33]. It seems to be a potential reason why BIF for HAN is higher than for THM for WTP Raba network.

The distribution of individual compounds from HK group is presented in Fig. 5(A) for WTP Raba distribution system and in Fig. 5(B) for WTP Bielany. HK share in both systems was similar. 1, 1-DCP constituted 48% of HK in WTP Raba distribution system, and 45% in WTP Bielany one. The share of 1,1,1-TCP was, respectively, 52% and 55%.

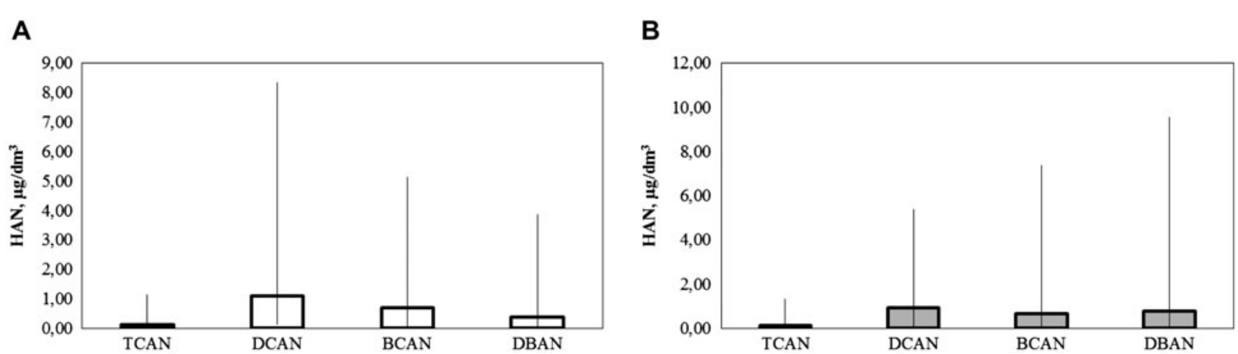

Fig. 4. The concentration of individual compounds in HAN group in the water distribution system of: (A) WTP Raba and (B) WTP Bielany.

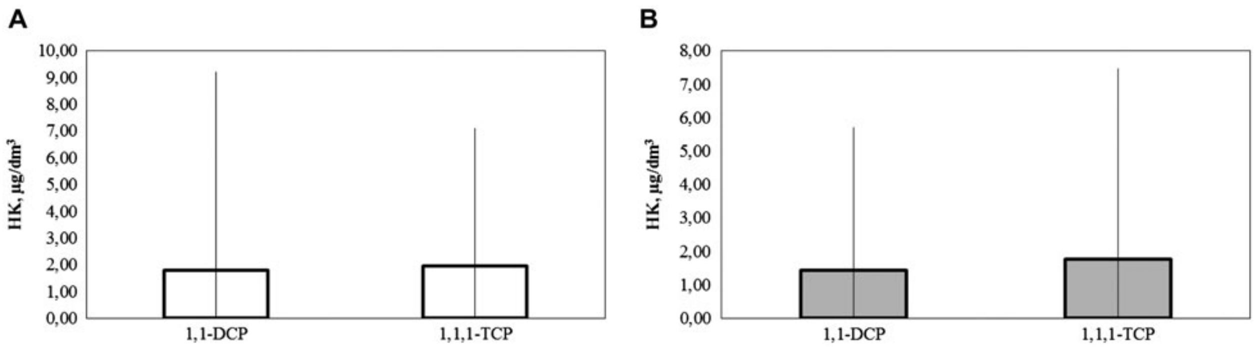

Fig. 5. The concentration of individual compounds in HK group in the water distribution system of: (A) WTP Raba and (B) WTP Bielany.

4. Conclusions

The research on the occurrence of volatile organic chlorination by-products in water distribution systems supplied by WTP Raba and WTP Bielany allows one to form the following conclusions:

- Despite better parameters of raw water, the average concentration of volatile chlorination by-products in WTP Raba distribution system was 15% higher when compared with WTP Bielany one. It is probably caused by the bigger size of Raba network and the need of additional water chlorination in the network.
- The highest share among all analyzed VCBPs in both networks had THM (70.5% in WTP Raba and 69.4% in WTP Bielany) and HK (12.5% for both networks); due to higher concentration of organic nitrogen in water from WTP Bielany the share of HAN in this network (9.5%) was higher than in WTP Raba network (7.7%); CH had 9.1% share of all analyzed DBPs in water from WTP Raba network, while in WTP Bielany it was 8.2%; CP had the lowest share in both systems; 0.3% for WTP Raba and 0.4% for WTP Bielany.
- Regarding the distribution of brominated compounds in individual groups of DBPs, water from WTP Bielany, due to higher concentration of bromide in raw water, was characterized by a higher share of brominated VCBPs when compared to their equivalents in water from WTP Raba.
- TCM was generated in the higher amount, among compounds from THM group, in both distribution systems (75% of all THM in WTP Raba system and 40% in WTP Bielany); DCAN had the highest share from all analyzed HAN both in WTP Raba system (48%), and in WTP Bielany one (38%); 1,1,1-TCP had the highest share among HK (52% for WTP Raba network and 55% for WTP Bielany one).

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