THE INFLUENCE OF ORGANIC MATTER QUALITY ON THE POTENTIAL OF VOLATILE ORGANIC WATER CHLORINATION PRODUCTS FORMATION

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Abstract: The paper presents the results of experiments on the influence of the organic matter's characteristics on the formation potential of water chlorination by-products – representatives of the following groups: trihalomethanes, haloacetonitriles, haloketones, chloral hydrate and chloropicrin. The products of water fractionation (the hydrophobic and hydrophilic acids, hydrophobic and hydrophilic bases, and hydrophobic and hydrophilic neutral fractions) were chlorinated with sodium hypochlorite. Its dose was adjusted to obtain a residual free chlorine concentration between 3 and 5 mg/dm³ after 24 h. After this time, the water chlorination by-products were analyzed with gas chromatography. The results' analysis has defined the fractions, which have the highest potential to form particular groups of volatile organic water chlorination by-products.

INTRODUCTION

Natural organic matter (NOM) commonly occurs both in surface water and shallow groundwater – the main sources of potable water. NOM gives water taste, odour and colour, increases coagulant and disinfectant demand in water treatment process, and also consumes residual chlorine and contributes to microbial regrowth in the distribution system [4, 18]. In addition to this, NOM contained in water reacts with chlorine or other disinfectants, and is a precursor of the formation of the halogenated disinfection by-products (DBPs). Main DBPs in drinking water include trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), haloketones (HKs), chloral hydrate (CH) and chloropicrin (CP) [2, 7]. These compounds are of scientific interest, due to the health effects they may have on human beings. Their concentration depends on several factors, such as chlorine dose, pH, temperature, bromide concentration as well as the concentration and characteristics of NOM [15]. To examine and describe the NOM characteristics, researchers often use the parameter $SUVA_{254}$ (specific UV_{254} absorbance – UV absorbance divided by the DOC concentration).The hydrophobic, aromatic and high molecular weight fractions of NOM (such as humic and fulvic acids) cause higher ultraviolet absorbance (UV_{254}) and higher SUVA, while the hydrophilic fractions of NOM cause lower UV_{254} and lower SUVA[1, 3].

The other way of characterizing the quality of organic matter is the fractionation method developed by Leenheer [8] and modified by several authors [6, 8, 10]. In this method NOM is fractionated on the ion exchange resins into six fractions: hydrophobic acid (HPOA), hydrophobic base (HPOB), hydrophobic neutral (HPON), hydrophilic acid (HPIA), hydrophilic base (HPIB) and hydrophilic neutral (HPIN). These fractions contain the following organic compounds [6, 9, 17]:

–   HPOA – aliphatic carboxylic acids (C5–C9), 1- and 2-ring aromatic carboxylic acids, aromatic acids, 1 and 2-ring phenols, tannins, soil fulvic and humicacids;
–   HPOB – portion of the humic substances retained by DAX-8 resin at pH ≈ 7 which can be eluted by hydrochloric acid; proteins, 1 and 2-ring aromatic amines (except pyridine), and high molecular weight alkyl;
–   HPON – hydrocarbons; aliphatic alcohols (> C5), amides, esters, ketones, aldehydes; long chain aliphatic carboxylic acids and amines (> C9); 3-ring (and greater) aromatic carboxylic acids and amines;
–   HPIA – aliphatic carboxylix acids (< C5) hydroxyl acids, sugars, low molecular weight alkyl monocarboxylic and dicarboxylix acids;
–   HPIB – aliphatic amines (< C9), amino acids, pyridines, purines, pyrimidines, low molecular weight alkyl amines;
–   HPIN – alcohols, aldehydes, esters, ketones, aliphatic amines (< C5); polysaccharides.

Fractionation allows for an evaluation of a potential risk of DBPs formation from each organic fraction present in the water sample.

The aim of this article is to define the precursors of several volatile water chlorination by-products, such us: THMs – trichloromethane (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM), tribromomethane(TBM); HANs – trichloroacetonitryle (TCA), dichloroacetonitryle (DCA), bromochloroacetonitryle (BCA), dibromoacetonitryle (DBA); HKs – 1,1-dichloroproponone (1,1-DCP), 1,1,1-trichloropropanone (1,1,1-TCP); CH and CP.

MATERIALS AND METHODS

Samples

The water samples for the experiments were taken from rivers in the city of Krakow: the Dłubnia, the Wilga and the Wisła. The samples were prepared by filtering through a 0.45 µm membrane filter and stored in darkness in temperature 4°C not longer than 24 h before fractionation.

Fractionation procedure

In order to conduct the NOM fractionation the modified fractionation procedure proposed by Marhaba *et al.* [10, 12] was used. Marhaba et al. has developed the method proposed by Leenheer [8] – they replaced one nonionic resin with three resins to eliminate the bleeding of organic substances. It allows to fraction reliably samples with low concentration of NOM (< 5 mg DOC/dm^3). The isolation of each NOM fraction was performed through adsorption using three types of resin: DAX-8 – nonionic resin (Supelco); AG-MP 50 – cationic resin (Bio-Rad); WA-10 – weak anionic resin (Supelco). The NOM fractionation was carried out using small (about 8 ml) resin volumes packed into glass column to fraction 500-ml water samples [11, 14]. Before their filling into the glass columns, they were conditioned in 0.1 M NaOH for 24 h, and then extracted sequentially for 24 h with

methanol-acetone-methanol using the Soxhlet extraction unit [6]. The packed resin was rinsed with high purity water until the conductivity was lower than 2 µS/cm. Before each experiment, the resins were rinsed with 100 cm³ 0.1 N NaOH and 100 cm³ 0.1 N HCl and 300 cm³ of water. The fractionation was conducted as follows (Fig. 1) [11, 12]:

1. The sample was filtered through a 0.45 µm membrane filter, adjusted to pH 7 and passed through the first column with DAX-8 resin; the hydrophobic neutral fraction was extracted by ethanol (POCh, anhydrous, 99.8%), which after that was evaporated in 40˚C.
2. The effluent was adjusted to pH 10 and passed through the second column with DAX-8 resin; the hydrophobic base fraction was desorbed with 25 cm³ 0.1 N HCl.
3. The sample effluent was adjusted to pH 2 and passed through the third DAX-8 resin column; the hydrophobic acid fraction was eluted with 25 cm³ 0.1 N NaOH.
4. The effluent was passed through the column with AG-MP-50 resin; the hydrophilic base fraction was eluted with 25 cm³ 1 N NaOH.
5. The sample effluent was passed through the column with WA-10 resin; the hydrophilic acid fraction was eluted with 25 cm³ 0.1 N NaOH.
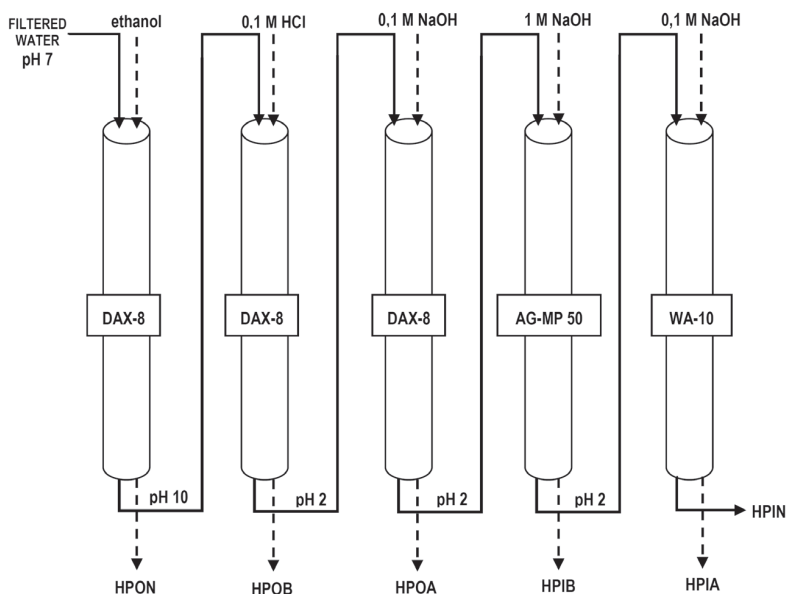6. The hydroplic neutral fraction is an effluent, which has flown through all columns.

Figure 1. NOM fractionation procedure

Water, during its fractionation, was flowing through the columns with gravity. After the elution process was finished, the samples were filled with water up to 500 cm³. Thus, one water sample produced six samples with fractionated organic compounds. DOC and DON (dissolved organic nitrogen) were analyzed in these samples.

Disinfection by-product formation potential

A 24 h chlorination test was carried out to examine disinfection by-products formation potential (FP). The samples of water were chlorinated using sodium hypochlorite solu-

tion. The chorine dosage for each water sample was determined so that a final residual chlorine of 3–5 mg/dm^3 remained in the sample after 24 h of incubation at 25°C. All samples were adjusted to pH 7 by adding sulphuric acid or sodium hydroxide and a phosphate buffer. A chlorinated water samples were incubated at 25 ± 2°C in amber bottles with PTFE liners.

Analytical methods

The volatile DBPs 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^{TM}-5ms capillary column (Restek) was used (film thickness 0.5 μm; column length 30 m; column diameter 0.25 mm). The THMs, HANs, HKs, CH and CP 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/dm^3.

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 of this method was 0.03 mg/dm^3.

The DOC was analyzed following Polish Standard PN-EN 1484. To oxidize organic matter the method of the chemical oxidation in fluid phase was applied (sodium persulfate/100°C) [5, 13]. CO_2, which was released in the process, was analyzed using the gas chromatograph with the Trace Ultra DSQII GC-MS mass spectrometer (Thermo Scientific). The method detection limit was 0.3 mg/dm^3.

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

The bromide ion concentration was determined by the spectophotometric 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.

RESULTS AND DISCUSSION

The results of the raw water analysis are shown in Table 1. The results of experiments on the formation of potential DBPs for the particular NOM fractions are shown in Table 2. The discussion on the results is presented below.

Table 1. Raw water characteristics

	DOC, mg/dm^3	DON, mg/dm^3	Br, mg/dm^3	UV$_{254}$, cm^{-1}	SUVA, cm^{-1}·dm^3/mg	pH
Dłubnia	12.55	4.80	0.2	0.183	0.015	8.01
Wilga	26.60	1.28	n.d.	0.672	0.025	7.74
Wisła	25.33	2.33	1.2	0.460	0.018	7.77

n.d. not detected

Table 2. The concentration of disinfection by-products and DOC and DON in each fraction

	Fraction					
	HPON	HPOB	HPOA	HPIB	HPIA	HPIN
DŁUBNIA						
TCM, µg/dm³	5.65	6.36	6.13	3.82	6.90	7.97
BDCM, µg/dm³	0.22	0.72	0.28	0.13	1.70	6.31
DBCM, µg/dm³	0.23	0.21	0.13	0.07	0.44	1.79
TBM, µg/dm³	0.08	n.d.	n.d.	n.d.	0.05	0.30
TCA, µg/dm³	0.01	0.01	0.02	0.02	0.01	0.01
DCA, µg/dm³	0.09	0.07	0.24	0.10	0.10	0.43
BCA, µg/dm³	0.27	0.08	0.29	0.34	0.15	0.29
DBA, µg/dm³	0.06	n.d.	0.10	0.01	0.01	0.12
1,1-DCP, µg/dm³	0.27	0.26	0.21	0.22	0.16	0.52
1,1,1-TCP, µg/dm³	0.09	0.25	1.79	1.28	0.29	1.40
CH, µg/dm³	1.36	1.31	1.30	1.15	5.81	2.58
CP, µg/dm³	n.d.	n.d.	0.01	0.06	0.04	n.d.
DOC, mg/dm³	1.04	2.63	1.76	0.87	1.37	3.44
DON, mg/dm³	0.03	0.05	0.17	0.17	0.39	3.72
WILGA						
TCM, µg/dm³	25.51	15.89	35.30	11.77	15.44	37.26
BDCM, µg/dm³	0.09	0.88	0.62	0.19	0.30	8.62
DBCM, µg/dm³	0.28	0.34	0.08	0.09	0.53	6.56
TBM, µg/dm³	0.03	0.02	0.04	0.04	0.02	0.87
TCA, µg/dm³	0.01	0.07	0.01	0.02	0.01	0.01
DCA, µg/dm³	0.35	0.13	0.43	0.33	0.09	0.65
BCA, µg/dm³	0.22	0.51	0.10	0.15	0.19	0.22
DBA, µg/dm³	0.20	n.d.	n.d.	0.23	0.25	0.04
1,1-DCP, µg/dm³	0.38	0.60	0.53	0.62	0.94	1.01
1,1,1-TCP, µg/dm³	0.35	1.00	7.34	1.56	0.43	0.73
CH, µg/dm³	1.45	1.34	4.63	1.01	2.36	8.42
CP, µg/dm³	n.d.	0.04	0.04	0.08	0.02	0.01
DOC, mg/dmv	3.51	3.17	3.92	3.83	3.95	6.02
DON, mg/dm³	0.07	0.05	0.05	0.06	0.13	0.81
WISŁA						
TCM, µg/dm³	15.47	5.62	47.17	9.09	9.21	9.60
BDCM, µg/dm³	2.89	3.59	5.50	0.35	8.32	19.11
DBCM, µg/dm³	0.77	1.34	0.50	0.07	11.99	67.44
TBM, µg/dm³	0.28	0.28	0.20	0.15	9.52	52.67
TCA, µg/dm³	0.02	n.d.	n.d.	0.01	n.d.	0.02
DCA, µg/dm³	0.09	0.66	1.17	0.63	0.58	0.17
BCA, µg/dm³	0.27	0.18	0.08	0.16	0.16	0.09
DBA, µg/dm³	0.02	n.d.	0.05	0.04	0.03	0.11
1,1-DCP, µg/dm³	0.90	0.66	0.34	0.42	0.85	0.52
1,1,1-TCP, µg/dm³	0.38	0.18	0.13	0.28	0.29	0.23
CH, µg/dm³	3.68	2.04	3.54	2.09	0.52	1.65
CP, µg/dm³	0.01	0.08	0.02	0.19	0.03	0.02
DOC, mg/dm³	3.24	2.37	5.11	3.62	2.39	6.30
DON, mg/dmv	0.48	0.05	0.10	0.06	0.45	1.48

n.d. not detected

Raw Water

The water samples from the Wilga and Wisła rivers had similar values of DOC (26.60 mg/dm^3 and 25.33 mg/dm^3 respectively) and rather low values of DON (1.28 mg/dm^3 and 2.33 mg/dm^3), while water from the Dłubnia river had a relatively lower DOC concentration (12.55 mg/dm^3), but higher DON concentration (4.80 mg/dm^3). To assess the quality of organic matter, beside DON and DOC, the specific UV$_{254}$ absorbance was determined in each water sample. SUVA$_{254}$ is the UV absorbance divided by the DOC concentration. Water samples containing the hydrophobic, aromatic and high molecular weight fractions of NOM (such as humic and fulvic acids) have higher ultraviolet absorbance (UV$_{254}$) and higher SUVA, while the hydrophilic fractions of NOM cause lower UV$_{254}$ and lower SUVA. The analyzed raw water samples had very similar values of SUVA, however the lowest value was observed for the Dłubnia river (0.015 cm^{-1}·dm^3/mg), then for the Wisła river (0.018 cm^{-1}·dm^3/mg), and the highest for the Wilga river (0.025 cm^{-1}·dm^3/mg). As it can be observed in Table 1, the sample from the Wisła river had the highest bromide concentration (1.2 mg/dm^3), then one from the Dłubnia river (0.2 mg/dm^3), in the sample from the Wilga river bromide was not detected.

Regarding DOC in the organic matter fractions, in all analyzed samples higher values of hydrophobic fractions (51–57%) were observed than of hydrophilic ones (43–49%). The dominant fraction in the sample from the Dłubnia river was HPIN (31%). High levels were also observed for fractions: HPOB (24%), HPOA (16%) and HPIA (12%). The lowest share in organic matter of the Dłubnia river had HPON (9%) and HPIB (8%). Despite the fact that the resins were carefully prepared and eluted, some amount of contaminants from resins were eluted to the fractionated samples. The sum of DOC was 13% higher than in the original water sample. The resins bleeding reported in other papers was up to 15% [12]. For the Wilga river, among all analyzed fractions of organic matter, the most dominant one was HPIN (25%). Relatively high values were also observed for HPIB (16%) and HPIA (16%), while the hydrophobic fractions had lower concentrations: for HPOB it was 13%, HPON – 14%, HPOA – 16%. The sum of DOC in all fractions was about 9% higher than in water before the fractionation. In the water sample from the Wisła river the dominant fraction was also HPIN (27%). The high share was also observed for HPOA (22%), HPIB (16%) and HPON (14%). The lowest values for the Wisła river were observed for fractions HPIA (11%) and HPOB (10%). The sum of DOC in all fractions was about 10% higher than in water before the fractionation.

Regarding the organic nitrogen concentration in the separate fractions, definitely the highest values in all analyzed samples were observed for HPIN – it was 82% of all fractions in the sample from the Dłubnia river, 70% in the Wilga river, 68% for Wisła river. A relatively high share of HPIA fraction was also observed (8% for Dłubnia, 11% for Wilga and 21% for Wisła). The share of the other fractions was lower than 6%. Bleeding of the raisins for organic nitrogen was 6% to 10%.

THMs formation potential

The results of experiments on the total trihalomethanes (sum of TCM, BDCM, DBCM and TBM) formation potential (TTHMFP) for the particular fractions of NOM are presented in Figure 2A, and trichloromethane formation potential (TCMFP) in Figure 2B.

THMs were formed by all six NOM fractions. TTHMFP was between 2.7 and 23.6 µg/mg DOC. The highest values of THMFP were observed in the result of chlorination of HPIN fraction for the water sample from Wisła river (23.6 µg/mg DOC), HPOA for

A   **B**
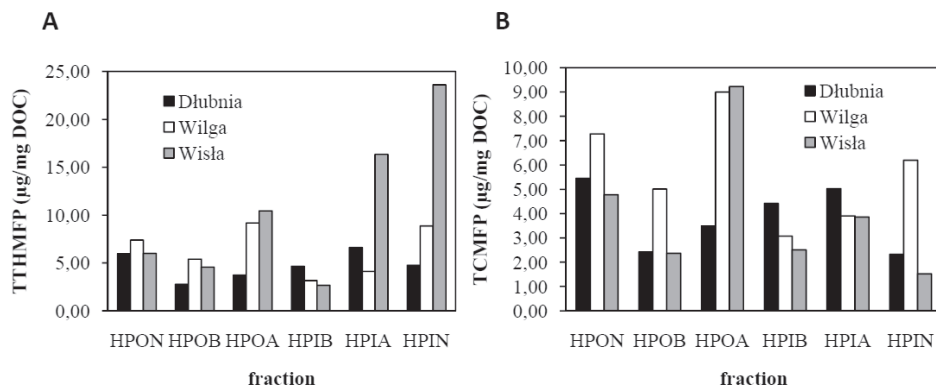

Figure 2. Trihalomethanes formation potential of organic fractions
(A) TTHMFP per DOC (B) TCMFP per DOC

the water sample from the Wilga river (9.2 µg/mg DOC) and HPIA for the water sample from the Dłubnia river (6.6 µg/mg DOC). The high concentration of TTHM in chlorinated fractions HPIN and HPIA from the Wisła river was caused by the high concentration of bromide derivatives of THMs (Table 2). Due to the applied NOM fractionation procedure, bromides were mainly present in the HPIN fraction, and it caused the high formation of brominated THMs by this fraction. Water from the Wisła river had a high concentration of bromide ion (1.2 mg/dm³) in comparison to other samples, and such high value of THMFP is caused mainly by high concentrations of BDCM, DBCM and TBM in the chlorinated samples. A similar research done by other authors have also proved the fractions HPIN, HPOA, HPOB and HPIA to have potential to generate THMs. Marhaba *et al.* [9] reported that HPOB fraction was the most reactive in formation of THMs followed by the HPIA fraction. In other reports [18] HPOA was marked out as the chemical fraction being the dominant THM precursor. Research conducted by Panyapinyopol *et al.*[12] showed that HPIN and HPOA fractions were two main precursors for THMs formation, but HPON and HPIN fractions only led to the formation of mostly TCM, while other organic fractions formed both TCM and BDCM. The research presented in this article also proved the role of HPON fraction in TCMFP, however, the dominant fraction in this process was HPOA.

HANs formation potential
Due to the presence of carbon and nitrogen atoms in the molecules of HANs, total haloacetonitriles (sum of TCA, DCA, BCA and DBA) formation potential (THANFP) was analyzed in regard to the organic carbon fractions (Figure 3A), and to the organic nitrogen fractions (Figure 3B).

THANFP was between 0.1 and 0.5 µg/mg DOC for the organic carbon fractions, and between 0.2 and 17.4 µg/mg DON for the organic nitrogen fractions. Among the organic nitrogen fractions, HPOB was found to contain most reactive precursors with regard to the THANFP (averagely for all tested samples). For this fraction the formation of HANs was highest for the water from the Wilga river (15.7 µg/mg DON) and for the water from the Wisła (17.4 µg/mg DON). THANFP for the water from the Dłubnia was highest for HPON fraction (13.9 µg/mg DON). The organic fractions of HPIA and HPIN were the groups with the lowest potential to form HANs (0.2–4.1 µg/mg DON).
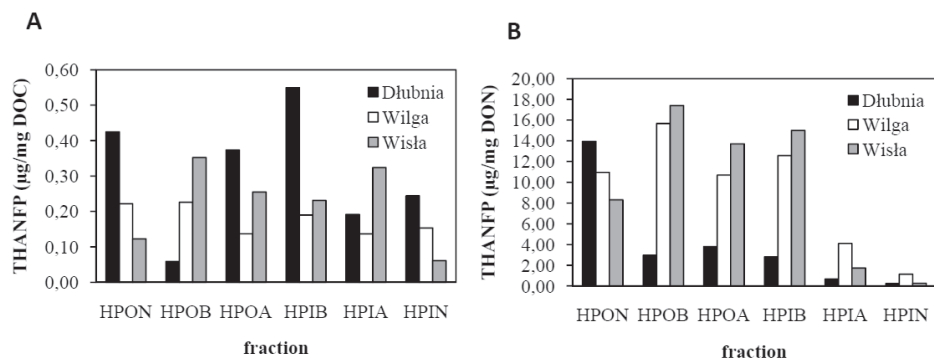
Figure 3. Haloacetonitriles formation potential of organic fractions
(A) THANFP per DOC (B) THANFP per DON

HKs formation potential

The result of research on the total haloketones (sum of 1,1,1-TCP and 1,1-DCP) formation potential (THKFP) for particular NOM fractions is presented in Figure 4A. For all the analyzed samples THKFP was low, between 0.1 and 2.0 µg/mg DOC. The highest values of THKFP were observed as the result of chlorination of HPOA fraction (averagely for all the tested samples). For the sample from the Dłubnia river the highest THKFP was obtained for HPIB (1.7 µg/mg DOC); from the Wilga – for HPOA (2.0 µg/mg DOC); and from the Wisła – for HPIA(0.5 µg/mg DOC).
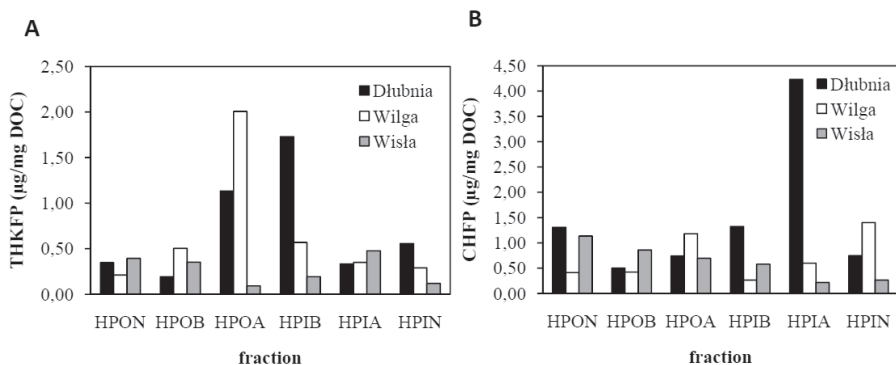

Figure 4. Haloketones and chloral hydrate formation potential of organic fractions
(A) THKFP per DOC (B) CHFP per DOC

CH formation potential

The results of the research on the chloral hydrate formation potential (CHFP) for particular NOM fractions are presented in Figure 4B. For all the analyzed samples CHFP was low, its values were between 0.2 and 4.2 µg/mg DOC. The highest values of CHFP were observed in the result of chlorination of HPON and HPOA (averagely for all tested samples). For the sample from the Dłubnia river the highest CHFP was obtained for HPIA fraction (4.2 µg/mg DOC); from the Wilga – for HPIN (1.4 µg/mg DOC); and from the Wisła – for HPON (1.1 µg/mg DOC).

CP formation potential

Chloropicrin (trichloronitromethane) has both nitrogen and carbon atoms in its molecule, thus its formation potential was analyzed in regard to both organic carbon fractions (Figure 5A) and nitrogen ones (Figure 5B).
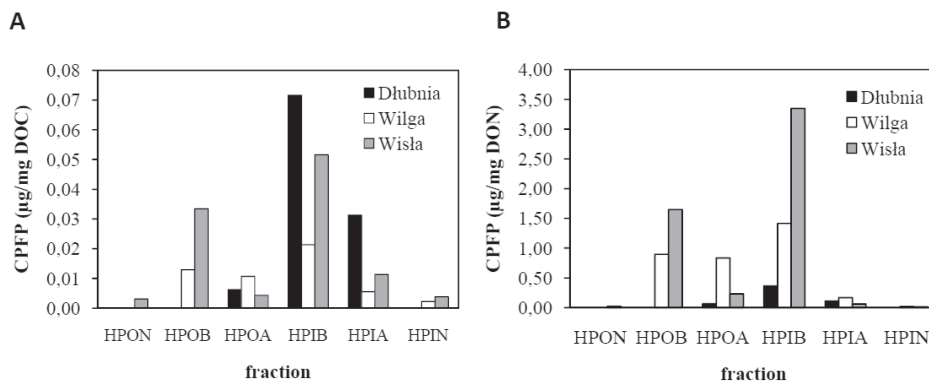

Figure 5. Chloropicrin formation potential of organic fractions
(A) CPFP per DOC (B) CPFP per DON

The HPIB fraction has the highest chloropicrin (CP) formation potential (CPFP) – the highest results of this parameter were obtained for all tested samples, both for carbon and nitrogen fractions. The fractions of HPIA and HPOA also contributed to CP formation, on the contrary the fractions of HPON and HPIN had no influence on CP formation, neither carbon nor nitrogen organic fractions. Generally in CP formation the nitrogen organic fractions played an important role, however, CPFP was very low, between 0.0–0.1 µg/mg DOC and 0.0–3.3 µg/mg DON. Such low values have the positive meaning because the toxicology studies showed that halonitromethans are the most cytotoxic and genotoxic among all DBPs, and have higher toxicity than regulated THMs [16].

CONCLUSIONS

Defining the precursors of DBPs formation plays an important role in the optimization of the water treatment technology. Combining the results presented in the article with those in numerous works on the dynamics of organic matter fractions removal in the water treatment process, e.g. [12], a selection of raw water sources and/or the treatment process modification can be used to minimize the water chlorination by-products. The results of the experiments presented in the article allowed to identify the groups of organic compounds, which have the highest potential to form the water chlorination by-products from the following groups: trihalomethanes, haloacetonitriles, haloketones, chloral hydrate and chloropicrin.

The investigation performed have led to the following conclusions:

– TTHMFP was the highest for all tested groups, its observed levels were in a range from 2.7 to 23.6 µg/mg DOC; THMs were formed by all six fractions, however, the dominant ones were HPIN, HPOA and HPIA; the high THMs formation potential

of HPIN fraction was caused by the bromides presented in it; hydrophobic acid and neutral fractions contributed to TCM formation;

– THANFP was from 0.1 to 0.5 µg/mg DOC and from 0.2 to 17.4 µg/mg DON; HPOB fraction was found to contain most reactive precursors with regard to the FP of THANs;

– THKFP was low (0.1–2.0 µg/mg DOC); the highest HKs formation potential was observed as the result of the chlorination of HPOA, HPIB and HPIA fractions;

– CHFP was low (0.2–4.2 µg/mg DOC); the highest CHFP was observed as the result of the chlorination of HPIA, HPIN and HPON fractions;

– The nitrogen organic fractions played the most important role in CP formation; CP has the lowest formation potential among all the tested groups; CPFP was 0.0–0.1 µg/mg DOC and 0.0–3.3 µg/mg DON; the carbon and nitrogen organic hydrophilic bases have contributed the most to CP formation; neither carbon nor nitrogen HPON and HPIN fractions took part in CP formation.

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WPŁYW JAKOŚCI MATERII ORGANICZNEJ NA POTENCJAŁ TWORZENIA SIĘ LOTNYCH ORGANICZNYCH PRODUKTÓW CHLOROWANIA WODY

W artykule przedstawiono wyniki badań nad wpływem jakości materii organicznej na potencjał tworzenia się produktów ubocznych chlorowania wody z grupy trihalometanów, haloacetonitryli, haloketonów oraz wodzianu chloralu i chloropikryny. Badania przeprowadzono na próbkach wody rzecznej, pobranej w okolicach miasta Krakowa. Materia organiczna każdej próbki wody została rozdzielona na sześć frakcji na trzech typach złóż jonitowych (DAX-8, AG-MP-50 i WA-10). Otrzymane w wyniku rozdziału kwasy hydrofobowe i hydrofilowe, zasady hydrofobowe i hydrofilowe, a także obojętne frakcje hydrofobowe i hydrofilowe chlorowano podchlorynem sodu, taką dawką żeby uzyskać 3–5 mg/l pozostałego chloru wolnego po 24 h. Po tym czasie za pomocą chromatografii gazowej oznaczano powstałe produkty uboczne chlorowania wody. Analiza otrzymanych wyników pozwoliła wytypować frakcje, które charakteryzują się największym powinowactwem do tworzenia się poszczególnych grup lotnych organicznych produktów ubocznych chlorowania wody.