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The change in fractions of organic substances in water in the intermediate oxidation process

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ABSTRACT

This article presents the results of a study on the changes in the content of both biodegradable and non-biodegradable fractions of dissolved total organic carbon. The studies were conducted on a technical scale in surface and mixed water (underground water after aeration mixed with surface water after micro sieve) purification plants, and the oxidation process was performed with ozone and a mixture of chlorine and chlorine dioxide, respectively. The study demonstrated a significant increase in the biodegradability of organic substances in the oxidation process regardless of the type of oxidant used. Ozone turned out to be the most effective oxidant in eliminating and transforming organic substances, compared with chlorine and chlorine dioxide. In the case of the utilization of a mixture of chlorine and chlorine dioxide, a greater reactivity of chlorine dioxide with organic matter, especially refractive substances, was determined. In both water treatment plants, the transformation of high molecular weight organic substances to smaller ones dominated over the mineralization of total organic carbon. The type and size of the transformation of organic matter depended mainly on the type of oxidant utilized, and not on the level of water contamination.

Keywords: Degradation; Mineralization; Oxidation; Chlorine; Chlorine dioxide; Ozone; Biodegradable dissolved organic carbon; Organic substance fractions

1. Introduction

Effective elimination of organic substances from surface water requires the use of complex purification systems. In conventional water treatment systems, it is possible to eliminate effectively non-dissolved or high molecular weight dissolved organic compounds, including refractive compounds [1–3]. In order to increase the effectiveness of removal of organic substances, chemical oxidation processes are used [4], for which powerful oxidants are utilized chlorine, chlorine dioxide, and ozone. They assure a low level of mineralization of organic substances, and mainly cause the transformation of organic substances which leads to the formation of oxidation by-products. In the light of the possibility of the formation of oxidation by-products harmful to humans [5,6], ever more frequently, chlorine is replaced with chlorine dioxide or ozone. Thanks to the natural transformation of organic matter, the elimination of a significant portion of the chlorinated precursors of organic substances is

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achieved [7,8]. The success of the oxidation process, however, depends mainly on the place of its use in the technological system, and the type and dose of a chemical oxidant [9].

As has been repeatedly determined, the initial and/or intermediate oxidation leads to the formation of compounds with a much greater susceptibility to biodegradation by microorganisms [10,11]. Therefore, the use of this process is justified only in the case of the application of processes which eliminate organic substances of low molecular weight, such as biological substances, in a later stage of the water treatment process. This explains the frequent use of the ozonation process prior to filtration through a biologically active bed of granulated active carbon.

Due to the very complex and not entirely understood structure of natural organic matter, the effectiveness as well as the course of the oxidation process and/or of disinfection is different in various regions of the world [8] and, as shown by Taha et al. [12], it depends on the structure of the organic substances contained in the treated water. Therefore, the impact of the oxidation process on the changes in structure and the organic substance content in water is varied, and should be determined for the given type of water.

The goal of the presented study was to determine the changes in the content of organic substance fractions in the process of intermediate oxidation using ozone as well as a mixture of chlorine and chlorine dioxide on a technical scale.

2. Study subject and methodology

The study of the change in concentration of fractions of organic substances was carried out in technical conditions in two water treatment plants, namely a surface water treatment plant (SWTP) and a mixed water treatment plant (MWTP), constituting a mix of surface water after microsieve with aerated ground water. For the purposes of intermediate oxidation in the SWTP, an ozonation process was conducted following the coagulation, sedimentation, and sand filtration. The ozone dose throughout the study fit in the range between 0.51 and 4.60 g O_3/m^3, which corresponds to the dosages between 0.17 and 0.83 g O_3/g C. Ozonation was realized in ozonation chambers, in which the water contact with the oxidant was very long and fit in the range between 48.0 and 82.4 min.

In the MWTP, for the purposes of the process of oxidation, chlorine and chlorine dioxide were used; the oxidants were dosed at the same time to the pipeline transporting the water from the accelerators to the filter hall. For this reason, the intermediate oxidation in the MWTP occurred both at the time of water flow from the accelerators to the filter hall as well as during the time of water flow through rapid sand filters. Thanks to this, a long time of contact between the water and the oxidants was assured, ranging from 0.6 to 4.0 h.

The doses of oxidants ranged from 0.83 to 2.88 g Cl_2/m^3 and 0.24 to 0.60 g ClO_2/m^3, which corresponds to a dose of between 0.19 and 1.15 g Cl_2/g C (a dose of chlorine dioxide converted to an equivalent dose of chlorine).

In the study, the impact of the intermediate oxidation process on changes in dissolved biodegradable and non-biodegradable fractions of organic carbon was evaluated, making it possible to assess the impact of this process on the biodegradability of organic substances, and therefore also on the potential for secondary regrowth of microorganisms.

Samples for the analysis were collected both before and after the oxidation process, while maintaining the time of water flow through the apparatus. Water for the study was collected regularly in both plants once a month. In all samples, the concentration of total and dissolved organic carbon (TOC and DOC), biodegradable dissolved organic carbon (BDOC), ultraviolet absorbance, and oxidant remaining after processing with oxidants was marked.

The content of non-biodegradable dissolved organic carbon (NBDOC) was determined on the basis of the difference between DOC and BDOC. The concentration of TOC and DOC was determined by the use of a HACH LANGE IL 550 TOC TN analyzer, while the concentration of BDOC was determined using a modified version of Van der Kooij's method, as the difference between the content of dissolved organic carbon before and after incubation of the sample with flora characteristic to the water environment. Ultraviolet absorbance 254 nm was measured with a spectrophotometer produced by Schimadzu. The remaining oxidant concentration after oxidation was determined by the DPD method using a TurbFlex photometer produced by WTW company according to American Public Health Association, Standard methods for the examination of water and wastewater, 20th ed., Washington, DC, 1998.

The concentration of the remaining oxidants was measured at the place of collection of the water samples, and some other measurements were made after transporting the water in thermostatic conditions to the laboratory.

3. Results and discussion

Both the surface water as well as the mixed water which underwent chemical oxidation were characterized by a large variability of the organic substances content (Table 1), among which the dissolved fraction dominated, making up 47.1–100.0% and 56.8–98.8% of TOC.

Among the dissolved organic substances, the non-biodegradable fraction dominated, constituting precursors of chlorinated organic substances [13–15]. This, in the case of utilization of a mixture of chlorine and chlorine dioxide for intermediate oxidation (MWTP) increased the likelihood of formation of chlorinated organic substances at the stage of intermediate purification.

The dominant group of non-biodegradable substances were refractive substances, which is indicated by the determined (at a confidence level $\alpha = 0.05$) linear correlation between the content of NBDOC and the $\mathrm{UV}_{254}{}^{\mathrm{m}^{-1}}$ absorbance value in both waters: $\mathrm{NBDOC} = 0.231 \times \mathrm{UV}_{254} + 1.462$ (SWTP) ($R = 0.85$, $n = 24$) and $\mathrm{NBDOC} = 0.428 \times \mathrm{UV}_{254} + 0.273$ (MWTP) ($R = 0.87$, $n = 24$). However, the biodegradable fraction constituted merely 4.6–13.2% and 2.7–25.0% of DOC in surface and mixed water. Generally, a higher proportion of the biodegradable fraction—providing the potential for regrowth of microorganisms—characterized the mixed water (Fig. 1).

Mixed water was also characterized by higher concentrations of BDOC, which were on average close to 1,5 times larger than those determined in the surface water (Fig. 2).

In the process of intermediate oxidation, a very high consumption of oxidants was determined, which for ozone, due to the long time of residence of water in the ozonation chamber, it was 100.0%. For the chlorine-based oxidants, the consumption ranged from 67.8 to 95.0% and 48.0 to 78.0%, respectively, for chlorine and chlorine dioxide.

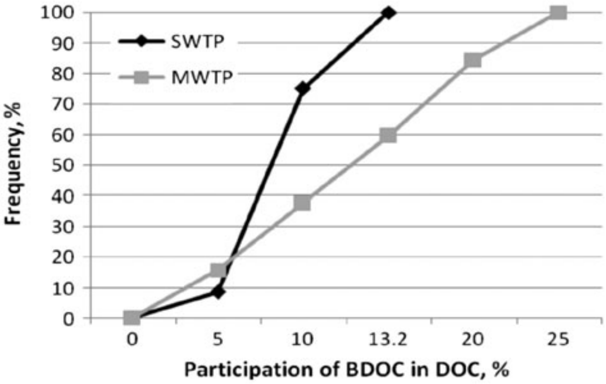

Fig. 1. Frequency of the occurrence of a particular biodegradable fraction in DOC.

Regardless of the type of oxidant used, the intermediate oxidation process caused a decrease in the content of dissolved and non-biodegradable organic substances (Fig. 3).

The effectiveness of removal of the dissolved non-biodegradable fraction was higher in reference to the surface water and its average value was 11.7 and 11.0% for DOC and 19.3 and 16.5% for NBDOC. The obtained effectiveness of removal of dissolved organic substances was close to that obtained by Zehra et al. [16], even though they use higher dosages of ozone. Nevertheless, there is a lack of information regarding the effectiveness of removal of DOC using a mixture of chlorine and chlorine dioxide. Shi et al. [17] demonstrated, however, that the use of $\mathrm{ClO_2}$ before chlorination allows for a 25–37% lower potential of creating THMs (and consequently a reduction in the

Table 1
Ranges of organic matter content before and after the intermediate oxidation process

		SWTP				MWTP			
		Before oxidation		After oxidation		Before oxidation		After oxidation	
Parameter	Unit	min	max	min	max	min	max	min	max
TOC	$\mathrm{gC/m^3}$	1.63	6.91	1.25	6.80	2.28	6.31	2.05	5.38
DOC	$\mathrm{gC/m^3}$	1.45	5.88	1.15	5.77	1.34	5.98	1.12	5.19
BDOC	$\mathrm{gC/m^3}$	0.16	0.44	0.28	0.75	0.11	0.86	0.19	1.08
NBDOC	$\mathrm{gC/m^3}$	1.27	5.48	0.85	5.02	1.19	5.14	0.93	4.56
$\mathrm{UV}_{254}{}^{\mathrm{m}^{-1}}$		4.06	15.62	2.82	9.70	2.75	12.70	1.50	11.80
$\mathrm{Cl_2}$	$\mathrm{gCl_2/m^3}$	–	–	–	–	0.83	2.88	0.28	2.08
$\mathrm{ClO_2}$	$\mathrm{gClO_2/m^3}$	–	–	–	–	0.24	0.60	0.00	0.51
$\mathrm{O_3}$	$\mathrm{gO_3/m^3}$	0.51	4.60	0.00	0.00	–	–	–	–

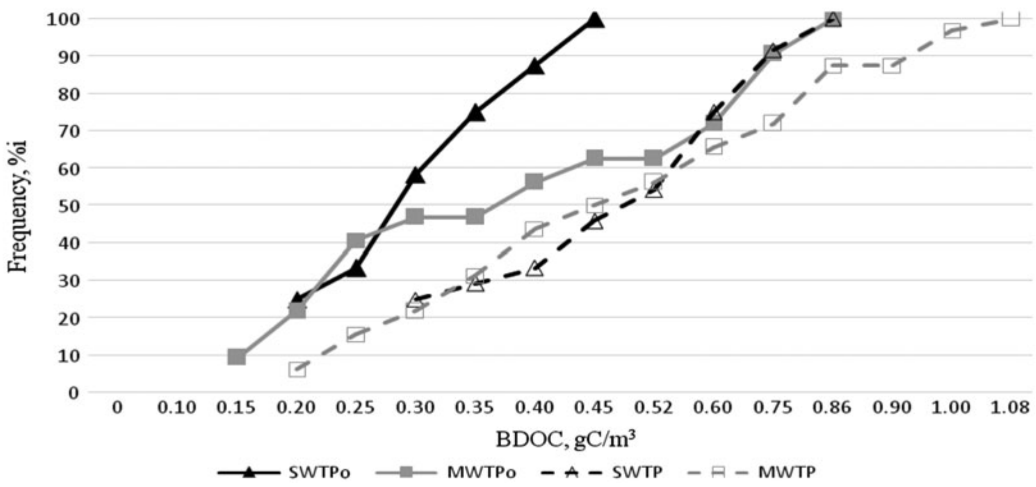

Fig. 2. Frequency of the occurrence of BDOC in surface and mixed water ($SWTP_0$ and $MWTP_0$ are BDOC concentration before the oxidation process).

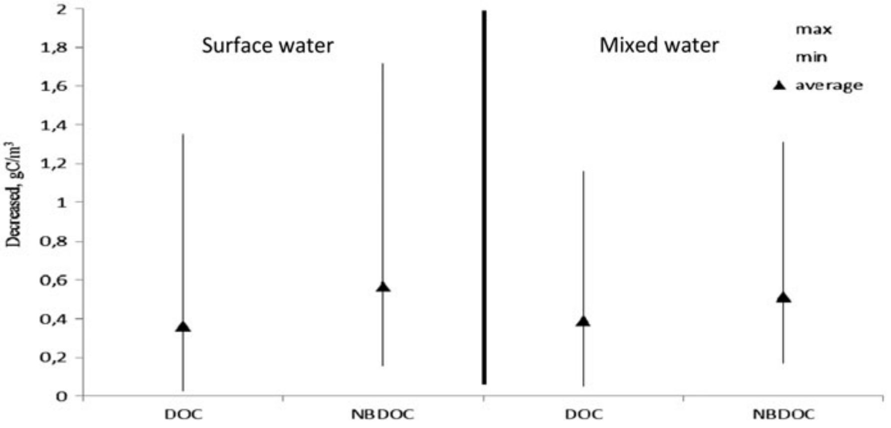

Fig. 3. Ranges and average of decrease in fractions of organic substances in the chemical oxidation process.

concentration of refractive substances), which greatly surpasses the values obtained in the present study. This may have been caused by the mutual interaction between chlorine and chlorine dioxide, and therefore by the decrease in the actual dose of oxidants.

In all the samples of surface water and mixed water, a larger decrease in the concentration of NBDOC as compared to DOC was determined, which indicates the formation of intermediate oxidation by-products.

In all samples of surface water, as well as mixed water, an increase in the concentration of BDOC was found, ranging from 0.05–0.46 to 0.01–0.40 g C/m^3. This was caused by the transformation of high molecular weight organic substances into more easily assimilable by microorganisms. This mechanism has been confirmed by the results of many studies [18,19]. A higher increase in the concentration of biodegradable organic substances was determined in relation to the less contaminated surface water. This is connected to the use of ozone, which according to Ali and Tarek [20] is a more effective oxidant than chlorine dioxide. This is also confirmed by the determined average increase in the content of biodegradable substances (69.8%) in surface water, which was nearly two times higher than the increase determined for mixed water (38.2%). The effectiveness of BDOC formation in both water treatment plants was small compared to the results obtained by Bond et al. [21], which demonstrate the low susceptibility of the natural organic matter (NOM) found in purified water to transformation into BDOC.

Irrespective of the type of oxidant used, the increase in the content of BDOC was greater the higher the initial content of NBDOC which characterized the water prior to undergoing the oxidation process (Fig. 4). A higher unitary increase in BDOC per 1 g of removed NBDOC was determined, however, in surface water, which also testifies to the greater reactivity of ozone than the mixture of chlorine and chlorine dioxide with NOM.

Among non-biodegradable substances undergoing transformation in mixed water, refractive substances dominated, which is confirmed by a linear correlation: $\Delta UV_{254}{}^{m^{-1}} = 3.1964 \times \Delta NBDOC - 1.6798$ ($R = 0.90$, $n = 24$). This relationship results from the high reactivity of chlorine dioxide with aromatic structures which has been confirmed in the studies of Yang et al. [22]. This dependence was not determined in relation to surface water, which can be explained by the higher reactivity of ozone and its lower selectivity.

Besides the transformation of organic substances, chemical oxidation also caused the mineralization of a portion of DOC. In 90.6% of MWTP water samples and 75.0% of SWTP samples, however, the dominant mechanism was that of transformation and not mineralization (Fig. 5), which amounted to 0.06–0.46 g C/m^3 and 0.01–0.40 g C/m^3 for SWTP and MWTP, accordingly. These results have been confirmed in other studies carried out around the world [23,24].

The quantity of organic substances subjected to mineralization in both plants was greater the higher the concentration of biodegradable organic substances found in the raw water (Fig. 6). Also in this case, the unitary degree of mineralization of organic substances was higher in relation to the surface water.

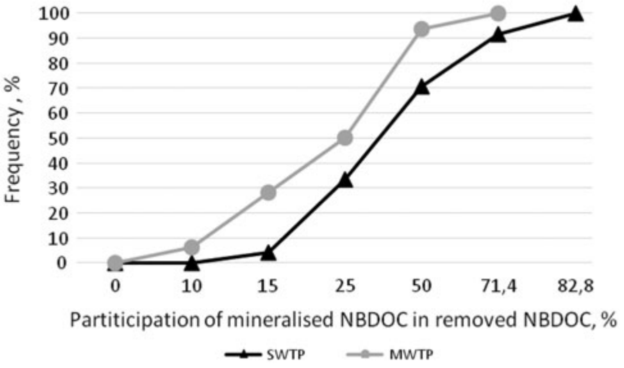

Fig. 5. Share of mineralization process in removing NBDOC.

The higher degree of mineralization of organic substances as a result of their oxidation by ozone rather than chlorine and chlorine dioxide is caused by higher reactivity of ozone as well as the fact, that in the case of utilizing chlorine, the formation of chlorinated organic substances is probable [17].

In contrast to the findings of studies [9,17], the impact of the time of contact of water with the oxidants on the effectiveness of the transformation or mineralization of organic substances was not determined in either of the discussed systems. This should be explained by the long time of contact of the water with the oxidants, which in the case of ozone results in its complete consumption while the water is still present in the ozonation chamber. In the case of the

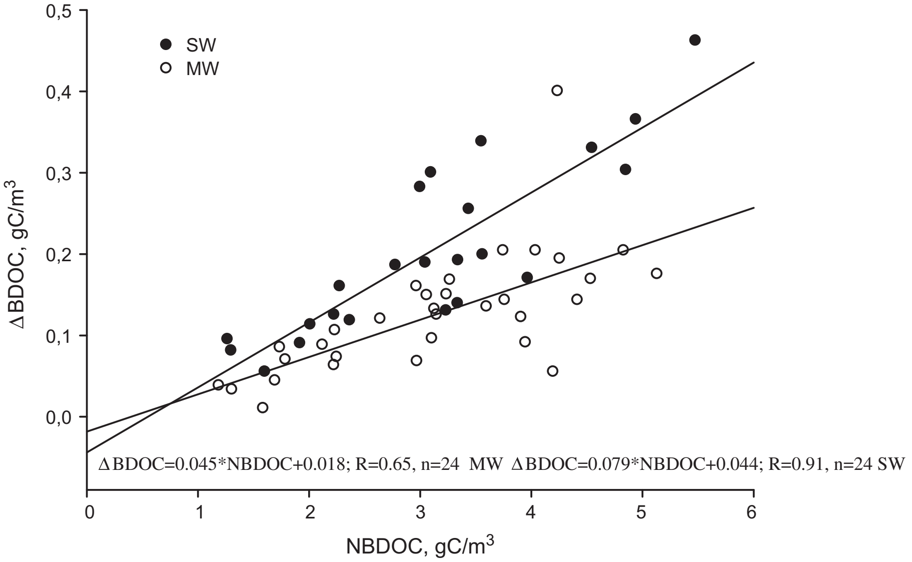

Fig. 4. Relationship between the content of non-biodegradable organic substances and the increase in the biodegradable fraction in the oxidation process.

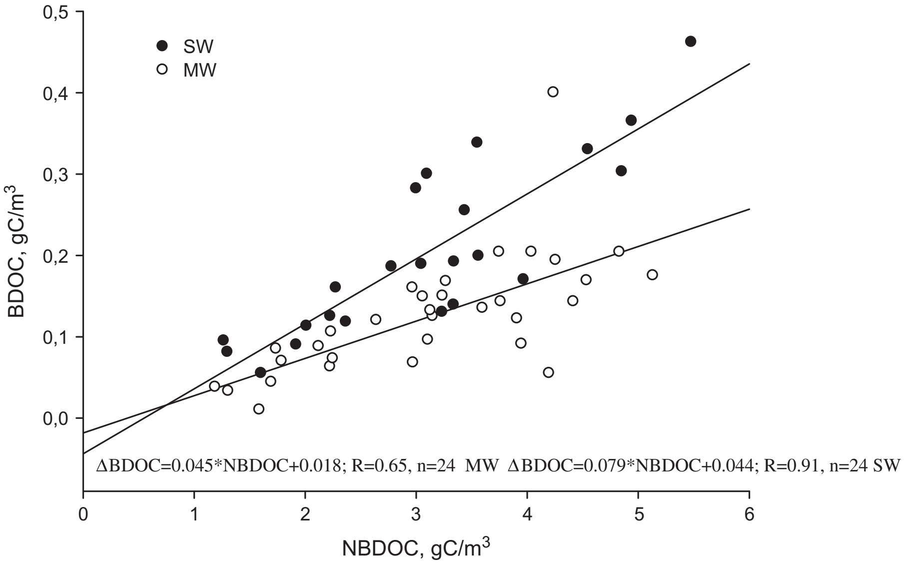

Fig. 6. The relationship between the content of NBDOC in waters undergoing oxidation and the quantity of mineralized organic matter.

use of chlorine and chlorine dioxide, however, this can result from their mutual interaction and/or varied reactivity of these oxidants with NOM. Additionally, it is important that chlorine reacts very slowly and requires a contact time of even a few dozen hours.

Reungot et al. [23] demonstrated that the effective dose of ozone needed to remove organic substances is 2.0–3.0 g O_3/g C, which means that in the analyzed system, the doses utilized (0.18–0.73 g O_3/g C) were too small. It is this small dose of ozone which can explain the lack of a relationship between the effectiveness of the transformation or mineralization of organic substances and the dose of ozone.

An increase in the effectiveness of transformation of organic substances in the elimination of NBDOC was, however, determined along with an increase in the dose of chlorine dioxide (participation of transformed NBDOC = 121.49 × D_{ClO2} + 24.95; $R = 0.82$, $n = 24$). This

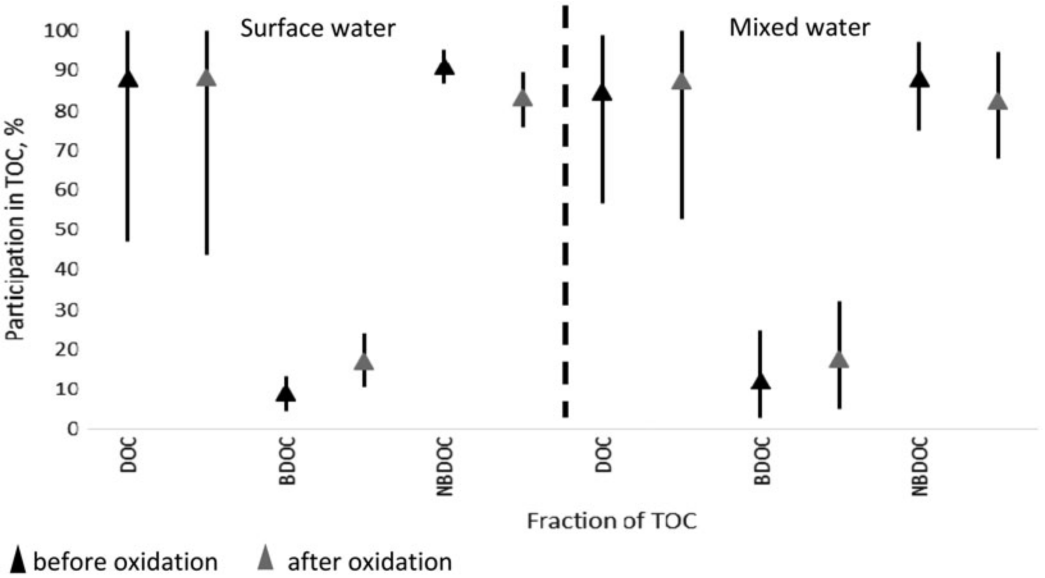

Fig. 7. Share of fractions of organic substances before and after intermediate oxidation.

is due to the greater potential of formation of biodegradable substances as a result of the reaction of organic matter with chlorine dioxide than with free chlorine, determined already by Ali and Tarek [20]. This indicates the decisive influence of the dose of chlorine dioxide on the course and effectiveness of the transformation of organic substances.

The result of the oxidation process in both plants was a decrease in the concentration of total organic carbon which amounted to 11.2 and 13.6% for the SWTP and MWTP, accordingly. After the oxidation process, an increase in the share of DOC in TOC was determined in 45.8 and 84.7% of water samples, which can indicate a process of transformation of non-dissolved organic substances into dissolved organic substances, which did not undergo mineralization. The changes in the share of concentration of dissolved organic carbon were not large, however, and for surface water, they amounted to a maximum of 4.1%, whereas in the mixed water, the value exceeded 5.5% in only one sample. A greater increase in the share of the dissolved fraction in the mixed water was probably caused by the smaller share of DOC in TOC in water subjected to this process.

In all water samples, a significant increase in the share of BDOC in DOC (Fig. 7) was determined, ranging between 3.8 and 11.5% and 2.3–15.4% for surface and mixed water. This increase was accompanied by a decrease in the share of non-biodegradable substances, which in the surface water corresponded to the increase in the share of BDOC. In the mixed water, the decrease in the share of NBDOC was smaller than the increase in the share of BDOC, which should be explained by the formation of halogenated organic substances.

4. Conclusions

(1) The intermediate oxidation process to a greater extent causes transformation and changes the distribution of the molecular weight of organic substances and it causes their mineralization.

(2) Changes in the structure of organic substances are mainly caused by the reaction of oxidants with non-biodegradable organic compounds, and in the case of chlorine dioxide particularly with refractive substances.

(3) The effectiveness of the mineralization of organic matter was directly proportional to the content of NBDOC in the water prior to the undergoing oxidation process.

(4) A more effective transformation of organic substances proceeded under the influence of ozone rather than the mixture of chlorine and chlorine dioxide.

(5) The quantity of biodegradable organic substances in the mixed water was proportional to the dose of chlorine dioxide, which determined the course of the process of transformation of organic substances.

(6) The effectiveness of the removal of organic substances depended primarily on the type of oxidant used, and to a much lesser extent on the level contamination of the treated water.

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