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Ozonation and Changes in Biodegradable Organic Substances in Drinking Water Treatment: The Future of Green Technology

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Abstract: Studies were carried out to assess changes in biodegradable dissolved organic carbon (BDOC) and assimilable organic carbon (AOC) in groundwater and surface waters after two processes: ozonation and ozonation/UV. The tested water was in contact with O_3 firstly for 4 and secondly for 15 min. Three doses of disinfectant were used: 1.6 mg/L, 5.0 mg/L, and 10.0 mg/L. The UV radiation time was 10 and 30 min. The greatest change in AOC and BDOC for groundwater was observed at an O_3 dose of 10.0 mg/L and a contact time of 15 min, by 400 and 197%, respectively. On the other hand, for surface water, it was shown that after the ozonation/UV process, the AOC and BDOC content decreased after both 10 and 30 min of radiation in comparison to the water after ozonation. The AOC content decreased by 33% and 22%, respectively, and the BDOC content by 27% and 31%, respectively. The results obtained in this study provide new information on the effect of different ozonation conditions and the combined method on the level of biodegradable organic fraction of water. It is recommended that BDOC and AOC should be monitored in Poland as routine indicators during the preparation of drinking water.

Keywords: assimilable organic carbon; biodegradable dissolved organic carbon; drinking water; ozonation process; UV radiation

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1. Introduction

The microbiological safety of water is the most important aspect in water treatment. Achieving biological stability requires water treatment that does not promote the growth of bacteria, taking into account the concentration of its nutrients and water distribution conditions that do not favour changes and the secondary growth of microorganisms, both in the water supply network and in internal installations [1]. Maintaining the microbiological safety of tap water in most large water supply systems is carried out through chemical disinfection. The usage of chemicals for water disinfection causes the formation of disinfection by-products (DBPs) [2–4]. Taking into consideration the wellbeing of consumers, a method of water treatment and disinfection is sought that would be free of water disinfection DBPs or their amount and type would not pose a significant health risk to the consumers. To measure overall water quality, total organic carbon and conductivity analyses are additionally introduced as surrogate measurements of overall water quality [5]. It is important to prepare water in the treatment process that is free of biodegradable organic substances when pumped into the water supply system [6–10]. AOC and biodegradable dissolved organic carbon (BDOC) can be a source of bacterial growth and development in the water treatment process. The biostability criterion is based on assessing the content of AOC or BDOC in water [7]. The phenomenon of the secondary development of microorganisms is primarily associated with the content of available organic carbon (AOC) [6–8]. AOC is part of the dissolved organic carbon (DOC). There is a difference between AOC and BDOC, because AOC is the part of DOC transformed into biomass, whereas BDOC is the difference

between the initial DOC and the minimum DOC reached during the bacterial growth period [11]. Therefore, it is preferable to determine AOC and compare it with BDOC to assess the biostability of water. Various cases and dependencies have been described in the literature, allowing for the formulation of a biostability criterion based on the AOC content in water pumped into the supply network [11]. However, the differences between the proposed AOC levels in water as a criterion suggest that other factors also affect the biostability of water in the distribution network. Water biostability depends on several factors, which include the content of readily biodegradable organic carbon compounds, temperature, and water residence time [12–16]. Other biological stability concepts have been described in the literature, that enable the highly effective analysis and in-depth characterisation of bacterial communities in drinking water; e.g., cell numbers by plate count (colony forming units/mL or CFUs) and/or confocal laser scanning microscopy (CLSM) measurements of the water before and after treatment can be performed [1,15,17].

Studies carried out in various countries, both in real and laboratory conditions, have shown the relationship between the degree of removal of natural organic matter in the treatment process and the amount of biodegradable organic substances formed as a result of the chemical disinfection of water [18]. Therefore, a thesis was formulated that the content of organic substances, including biodegradable fractions, depends on the type of disinfectant used and its dose. In Poland, so far, no water supply company takes into account the AOC and BDOC assays in the physicochemical analyses of water, despite the fact that organic carbon has the greatest impact on the development of the bacterial film formed in the water supply network. It is advisable to expand the range of monitored indicators by adding BDOC and AOC as routine parameters in practical devices for the preparation of drinking water. This is a proposal to develop risk assessment tools based on BDOC and AOC. Therefore, in light of the current legal changes, part of the research carried out is in response to the requirements regarding health risk assessment specified in Directive 2020/2184 of the European Parliament and of the Council (EU) of 16 December 2020 on the quality of water intended for human consumption [19]. At the same time, there is an increasing demand for green technologies that promote, among other things, sustainable water management [20]. Most climate change models in Poland predict an increase in air temperature in the coming years. However, a significant increase in precipitation is not forecast [21]. These phenomena may result in restrictions on water use and access to water services.

With respect to water resources, it is important to maintain the microbiological stability of drinking water. This approach will allow the selection of effective disinfection methods to prevent the secondary growth of microorganisms in the water supply network. Therefore, the aim of this research was to assess the qualitative and quantitative composition of organic substances represented by AOC and BDOC and to analyse the impact of the selected oxidant used in water treatment, i.e., O_3 and the combined ozonation/UV method, on the content of biodegradable organic carbon. As part of this work, the effect of different ozonation conditions (i.e., O_3 dose and the time of contact with water) and the combined method (ozonation/UV) on the levels of the biodegradable organic fraction was assessed on a laboratory scale for different types of raw water.

2. Materials and Methods

2.1. Materials

Water samples taken from a household well located in the city of Częstochowa with a population of 512,128 people and surface water from the Kozłowa Góra dam reservoir (GPS: N 50°25′46″ E 18°58′40″) located in the Silesian Voivodeship were used for the study.

Surface water is a common raw material in Poland used by water supply companies to produce drinking water. Water from the Kozłowa Góra dam reservoir is collected and treated by one water supply company in the Silesian Voivodeship. Water from the reservoir is purified using the raw water treatment technology, consisting of coagulation, rapid filtration, middle ozonation, and filtration through a bed of activated carbon.

Four water treatment plants operate in Częstochowa and the surrounding area, which treat water from intakes marked Wierzchowisko (W) (GPS: 50°53′27.9″ N 19°07′51.7″ E); Mirów (M) (GPS: 50°48′59.4″ N 19°10′29.3″ E); Łobodno (L) (50°56′00.5″ N 18°42′23.9″ E); and Rększowice (R) (GPS: 50°42′22.1″ N 19°01′49.9″ E). Water from the above intakes comes from wells with depths ranging from 37 m to 133 m (M), from 42 m to 71 m (W,) from 69 m to 90 m (L), and from a well 460 m deep (R).

In each of the drinking water production companies selected for the study, different technological processes are used to treat the raw water. In the disinfection of the produced water, different disinfectants and their different doses are used (Table 1).

Table 1. Treatment processes used for the tested waters taken from treatment plants.

Water Intake	Type of Disinfectant	Contact Time/Flow Rate
W	O_3 concentration - in the contact chamber 0.16 mgO_3/L ±0.05, - in water pumped into the distribution network 0.05 mgO_3/L ±0.01	9 min
M	O_3 disinfection O_3 concentration in the contact chamber 0.30 mgO_3/L ±0.05, - in water pumped into the distribution network 0.10 mgO_3/L ±0.01	17.5–27.5 min
L	Disinfection with the solution NaClO Disinfectant concentration 0.15 mgNaOCl/L	flow velocity in the contact chamber 15 m^3/h.
R	Disinfection with the solution NaClO Disinfectant concentration 0.16–0.17 mgNaOCl/L	flow velocity in the contact chamber 25 m^3/h.

The M intake has been operating since 1955 and is an intake where water is disinfected using ozonation. In the water treatment plant (WTP) W, water is treated using biological denitrification and its disinfection with the use of O_3. It is the oldest multi-hole underground water intake operated by the Water and Sewerage Company. Raw water is taken from wells (vertical underground water intakes, artificially drilled, reaching to the aquifer) and from a wellspring (natural, self-acting outflow of underground water to the terrain surface with a depth of 3 m). All water (from the wells and wellspring) is divided into two streams. About 50% of the water is supplied to the denitrification station, and the rest is run directly to the disinfection station using ozonation. In the water supplied to the treatment plant (biological denitrification), the process of reducing nitrates to gaseous nitrogen takes place. Then, the treated water is transported to the contact tank of the disinfection station, where, together with raw water pumped directly from the wells and wellspring, it is disinfected using O_3 produced in ozonators. In WTP L, water is disinfected with sodium hypochlorite. Water samples were collected according to standard methods [22]. A detailed preparation of model water is described in [23].

2.2. Methods

Analyses were carried out to determine the selected forms of organic carbon: total organic carbon (TOC), dissolved organic carbon (DOC), BDCO, and AOC before and after the disinfection process in the tested waters, i.e., model water, water taken from a household well, and water from a dam reservoir. The tests were carried out on a laboratory scale in an experimental installation, i.e., in the device for simulating disinfection processes.

The number of colonies of heterotrophic bacteria (number of colony forming units—CFU) in a fixed volume of water was also determined in the water samples. The details of the methodology are described in the literature [23].

Two stages of research were carried out. The first was to disinfect water samples with O_3. Ozone doses amounted to 1.6, 5.0, and 10.0 mg/L. When choosing O_3 doses, the real concentration of the disinfectant used in the Kozłowa Góra WTP, which is 1.7 mg/L, was taken into consideration. Additionally, a higher dose of 10.0 mg/L was used. Lower doses, similar to those used in the WTP in Częstochowa, could not be obtained in the ozonator used. The contact times were therefore adapted to the conditions prevailing in the Kozłowa Góra WTP and were set at 4 min and 15 min.

O_3 was produced from oxygen in a Korona L Spalab ozonator. O_3 was introduced into the water using an injector. The O_3 remaining in the water was removed using aeration. To determine the O_3 concentration, a method based on the reaction of O_3 with potassium iodide solution was used. Then, the separated iodine (in the presence of starch) was titrated with sodium thiosulfate to discolour. The accuracy of the iodometric method was ±1% for concentrations from 2 to 160 mgO_3/L.

In the second stage of the research, the impact of ozonation supported with UV radiation (ozonation/UV) on the content of TOC, DOC, AOC, and BDOC in water was analysed. The lowest dose of O_3 from the first stage was used, i.e., 1.6 mg/L, and the contact time of O_3 with water was 4 min. After the ozonation of the water, the UV radiation process was carried out. A UV_{254} low pressure lamp was used. The UV radiation time was 10 and 30 min [23].

For control purposes, tests were carried out to determine the content of selected forms of organic carbon, namely, TOC, DOC, BDCO, and AOC, in model water before and after disinfection processes (ozonation and ozonation/UV). TOC analysis, DOC analysis, BDOC analysis, and AOC analysis were carried out using procedures according to Rosińska and Rakocz [23].

3. Results

According to Standard the total number of microorganisms at 22 °C after 72 h must not exceed 100 CFU/mL in the water supply network [24]. Before the treatment process, water from the household well and water from the Kozłowa Góra reservoir demonstrated this parameter above the permissible value, amounting to 167 and 356 CFU/mL, respectively. In the water from the household well and water from the Kozłowa Góra reservoir after the treatment, this parameter was within the permissible value, at 15 and 25 CFU/mL, respectively.

3.1. The Impact of the Concentration and Contact Time of O_3 with Water on the Content of Selected Forms of Organic Carbon

Model water (a solution of humic acids) with a TOC content of 9.8 mgC/L was used as the first water to test the effect of the ozonation process and ozonation/UV on the content of selected carbon forms. The obtained results are presented in Table 2.

Table 2. TOC, DOC, AOC, and BDOC content (mg/L) in model water.

Organic Carbon Fraction	Raw Water	O_3 Dose						Ozonation/UV	
		1.6 mg/L		5.0 mg/L		10.0 mg/L			
		4 min	15 min	4 min	15 min	4 min	15 min	10 min	30 min
TOC	9.80	9.30	9.10	9.20	9.00	9.20	8.80	9.6	9.3
DOC	9.20	9.00	8.80	8.90	8.60	8.60	8.30	9.0	8.7
AOC	0.05	0.07	0.18	0.09	0.18	0.12	0.33	0.09	0.45
BDOC	0.25	0.44	0.56	0.50	0.56	0.62	0.75	0.30	0.36

It was shown that after applying three doses of O_3, the TOC content in the model water decreased, and with the increase in the contact time of the water with O_3, the TOC content also decreased. The largest decrease in the TOC content (by 10%) was recorded for the O_3 dose of 10 mg/L, after 15 min of water contact with the disinfectant. The same

relationship for model water was observed for DOC. The largest decrease in the content of DOC (by 10%) was also recorded for the O_3 dose of 10 mg/L after 15 min of water contact with the disinfectant.

In the case of AOC, the application of each of the three doses of O_3 increased the content of this indicator in the model water (Figure 1A). For the dose of 1.6 mg/L, after a contact time of 4 and 15 min, the AOC content increased by 40 and 260%, respectively. For the dose of 5.0 mg/L, after a contact time of 4 and 15 min, the AOC content increased by 80 and 260%, respectively. For the dose of 10.0 mg/L, the greatest change in the AOC content was shown, namely, 140 and 560%, respectively.

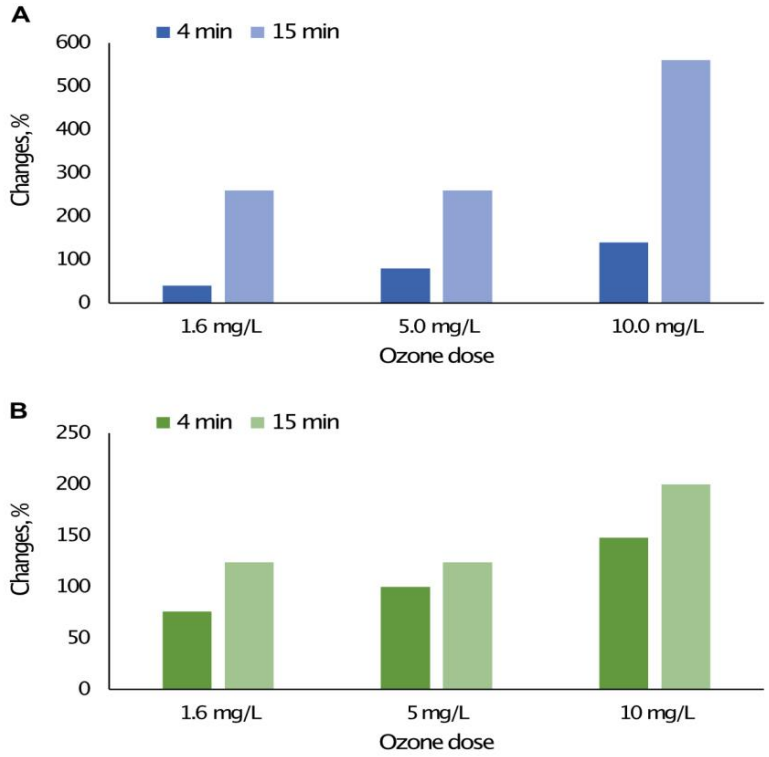

Figure 1. Changes in biodegradable organic substances in model water: (**A**) AOC, (**B**) BDOC.

In the case of BDOC, it was shown that with the increase in the dose and contact time, the content of this indicator in the tested water increased (Figure 1B). The smallest change in BDOC was observed at an O_3 dose of 1.6 mg/L and a contact time of 4 min (76% increase). At the same dose and a contact time of 15 min, the BDOC content increased by 124%. At a dose of 5.0 mg/L and a contact time of 4 and 15 min, the BDOC content increased by 100 and 124%, respectively. At a dose of 10.0 mg/L and a contact time of 4 min, the BDOC content increased by 124%, and at the same dose and a contact time of 15 min, the largest increase in the content of this indicator was observed (200%).

The contents of TOC, DOC, AOC, and BDOC in water taken from a household well located in the city of Częstochowa are presented in Table 3.

After administering the doses of 1.6 mg/L, 5.0 mg/L, and 10.0 mg/L, the concentration of TOC in the tested water decreased. The largest decrease (25%) was recorded for the dose of 10.0 mg/L O_3 and a contact time of 15 min. It was also shown that with increasing O_3 contact time with water, the TOC content decreased. A similar relationship was observed for DOC. After applying the dose of 1.6, 5.0, and 10.0 mg/L, the concentration of DOC in the tested water decreased. The largest decrease (18%) was recorded for the dose of 5.0 mg/L O_3 after a contact time of 15 min.

In the case of AOC, it was demonstrated that both with the increase in the O_3 dose and with the increase in the contact time, the content of this indicator in the tested water increased (Figure 2A). The smallest change in AOC was observed at the O_3 dose of 1.6 mg/L after a

contact time of 4 min (an increase of 29%). At the same dose and 15 min of contact time, the AOC content increased by 214%. At a dose of 5.0 mg/L and a contact time of 4 and 15 min, the AOC content increased by 71 and 243%, respectively. At a dose of 10.0 mg/L and a contact time of 4 and 15 min, the AOC content increased by 157 and 400%, respectively.

Table 3. TOC, DOC, AOC, and BDOC content (mg/L) in water from the household well.

Organic Carbon Fraction	Raw Water	O_3 Dose						Ozonation/UV	
		1.6 mg/L		5.0 mg/L		10.0 mg/L			
		4 min	15 min	4 min	15 min	4 min	15 min	10 min	15 min
TOC	13.05	11.50	11.10	10.86	10.65	9.84	9.79	11.44	11.26
DOC	11.65	10.42	9.85	9.65	9.55	10.02	9.88	10.98	10.77
AOC	0.07	0.09	0.22	0.12	0.24	0.18	0.35	0.11	0.15
BDOC	0.33	0.52	0.68	0.68	0.81	0.87	0.98	0.54	0.60

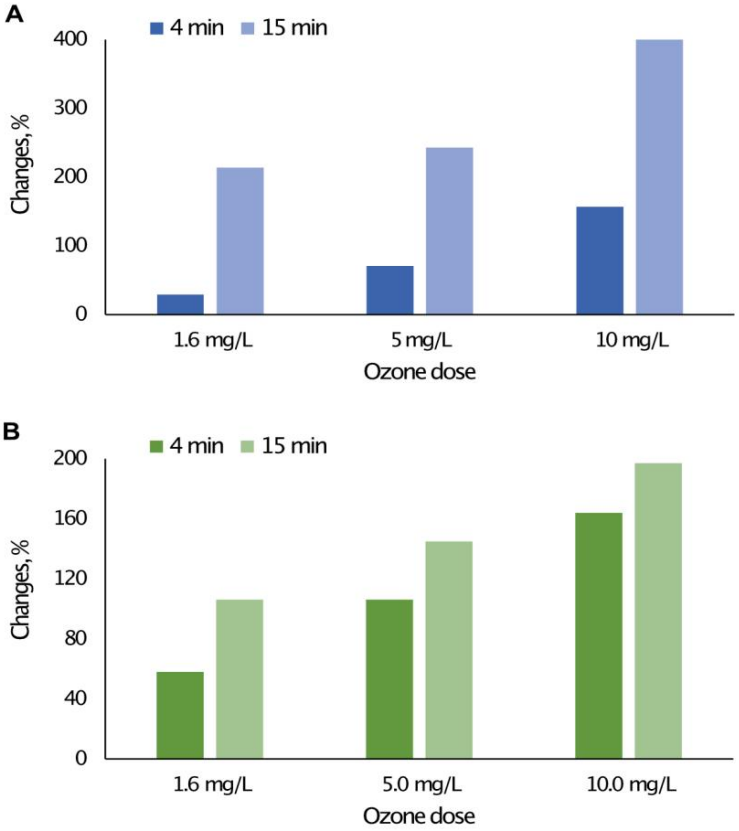

Figure 2. Changes in biodegradable organic substances in water from the household well: (**A**) AOC, (**B**) BDOC.

After analysing the content of BDOC in the tested water, it was proven that the concentration of this carbon fraction increased with an increase of the dose of O_3 and the time of contact. The BDOC changes in the tested water are shown in Figure 2B. After applying an O_3 dose of 1.6 mg/L and a contact time of 4 min and 15 min, the BDOC content increased by 58 and 106%, respectively. At a dose of 5.0 mg/L and a contact time of 4 and 15 min, the BDOC content increased accordingly by 106 and 145%. The most significant changes occurred at a dose of 10.0 mg/L and contact times of 4 and 5 min, with the indicator content increasing by 164% and 197%, respectively.

The contents of TOC, DOC, AOC, and BDOC after using different O_3 concentrations and different contact times in water from the Kozłowa Góra reservoir are presented in Table 4.

For the water taken from the Kozłowa Góra reservoir, similar changes in individual carbon fractions were observed as for the water taken from the well. After applying 1.6, 5.0, and 10.0 mg/L doses, the TOC levels decreased. With an increase in the contact time with O_3, the TOC content also decreased. The same relationship also applied to the content of DOC.

Table 4. TOC, DOC, AOC, and BDOC content (mg/L) in water from the dam reservoir.

Organic Carbon Fraction	Raw Water	O_3 Doze						Ozonation/UV	
		1.6 mg/L		5.0 mg/L		10.0 mg/L			
		4 min	15 min	4 min	15 min	4 min	15 min	10 min	30 min
TOC	13.02	12.20	12.00	12.12	11.98	11.85	11.56	11.45	11.23
DOC	10.68	10.00	9.85	9.85	9.83	9.82	9.78	10.34	9.96
AOC	0.060	0.090	0.120	0.100	0.140	0.100	0.160	0.06	0.07
BDOC	0.32	0.49	0.56	0.52	0.60	0.68	0.83	0.36	0.34

For water taken from the Kozłowa Góra reservoir, the concentration of AOC increased after the application of the three tested doses of O_3 (Figure 3A). It was shown that with an increase in the time of contact with O_3, the AOC content also increased. The smallest change (an increase of 50%) was observed for the O_3 dose of 1.6 mg/L after 4 min. For a dose of 1.6 mg/L and after a contact time of 15 min, the AOC content increased by 100%. For a dose of 5.0 mg/L and after 4 and 15 min, the AOC content increased by 67 and 133%, respectively. For a dose of 10.0 mg/L, after 4 and 15 min, the content of this indicator increased by 67 and 167%.

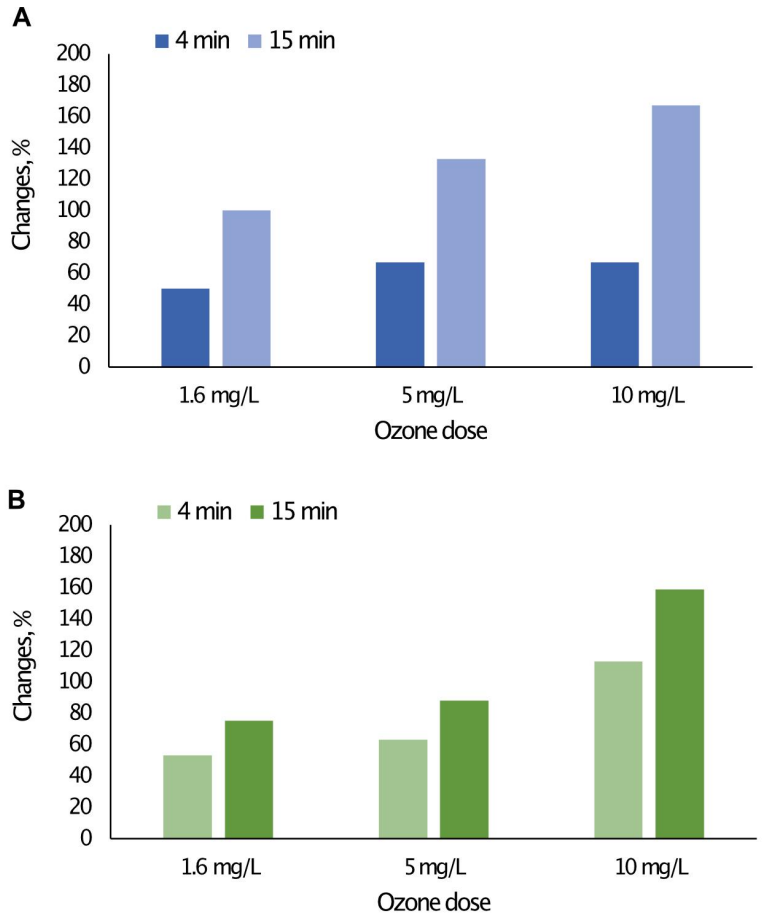

Figure 3. Changes in biodegradable organic substances in the dam reservoir: (**A**) AOC, (**B**) BDOC.

In the case of BDOC, the concentration of this carbon fraction increased with an increase in the O_3 dose and contact time (Figure 3B). The smallest increase in BDOC content (53%) was observed at a dose of 1.6 mg/L and a time of 4 min. For the same dose of O_3 after 15 min, the BDOC content increased by 75% compared to the BDOC content in raw water. For a dose of 5.0 mg/L O_3, an increase of 63 and 88% was shown after 4 and 15 min of contact, respectively, and for a dose of 10.0 mg/L after 4 and 15 min, BDOC increased by 113 and 159%, respectively.

3.2. Evaluation of Changes in the Content of Selected Forms of Organic Carbon in Water after the Process of Ozonation Assisted by UV Radiation

It was shown that after the application of the ozonation/UV process, the content of TOC in the model water decreased (Table 2). A similar relationship was observed for DOC. Supporting the ozonation with UV radiation resulted in an increase in the AOC content both after the contact time of 10 min and 30 min. The AOC content increased after 10 min of radiation by 27%, and after 30 min by 71% in relation to the AOC content in only ozonated water (Figure 4). For BDOC, the content was higher after radiation times of 10 and 30 min by 80 and 140%, respectively. The BDOC content after the ozonation/UV process after 10 and 30 min increased by 20 and 44%, respectively (Figure 4). The BDOC content after 10 and 30 min decreased by 32 and 18%, respectively.

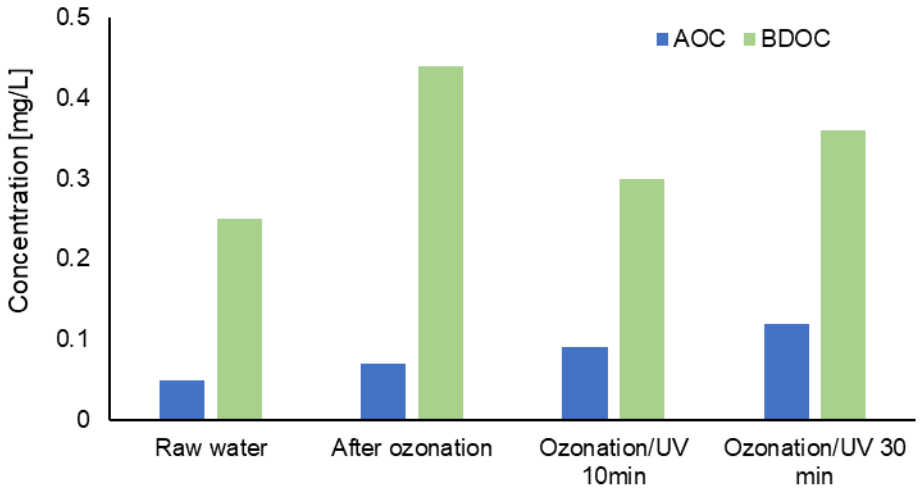

Figure 4. Concentrations of AOC and BDOC in model water after the ozonation/UV process.

For water taken from the well, after the ozonation/UV process, the content of TOC in the tested water decreased in relation to raw water and the water after ozonation process. The largest decrease in TOC content (14%) was observed in water after ozonation/UV disinfection for 30 min. The content of DOC after this disinfection process was lower than in raw water.

For both raw water and water after ozonation, supporting the ozonation process with UV radiation resulted in an increase in the AOC content (Table 3). The AOC content increased after 10 min of radiation by 57%, and after 30 min by 114% in relation to the AOC content in raw water (Figure 5). After ozonation and radiation with UV for 10 min, the AOC content increased by 22%, and after 30 min by 67%, in relation to the content of this parameter in the water after the ozonation process. The BDOC content after the ozonation/UV process after 10 and 30 min increased by 64% and 82%, respectively, in relation to the BDOC content in raw water (Figure 5).

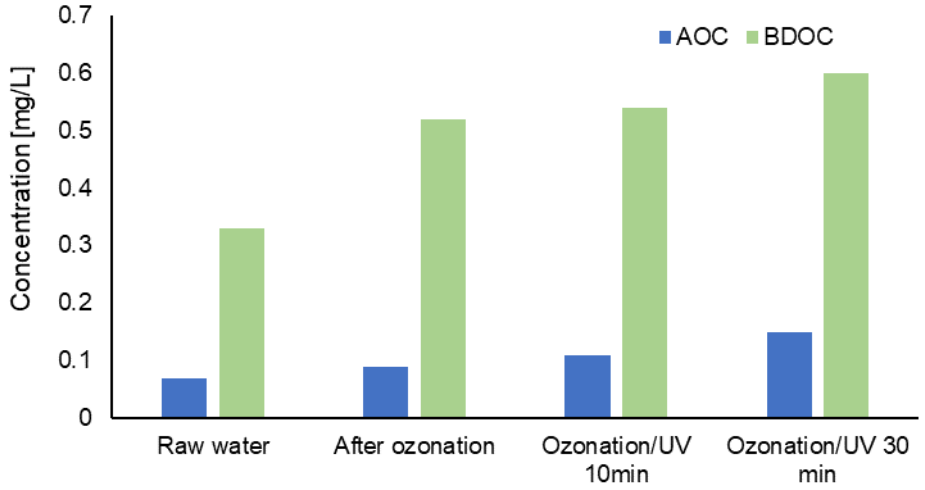

Figure 5. Concentrations of AOC and BDOC in water from the backyard well after the ozonation/UV process.

For water taken from the reservoir in Kozłowa Góra, it was demonstrated that after the ozonation/UV process, the content of TOC in the tested water decreased both in relation to raw water and the water after the ozonation process (Table 4). The largest decrease in the TOC content in relation to raw water (by 14%) was recorded for water after disinfection assisted by UV radiation for 30 min. The content of DOC after ozonation assisted by UV radiation was lower than in raw water.

The AOC content in relation to raw water increased by 17% after the ozonation/UV process after 30 min, while after 10 min the AOC content did not change (Figure 6). It was shown that the support of ozonation with UV radiation caused a decrease in the AOC content both after the contact time of 10 min and 30 min. The AOC content decreased after 10 min of radiation by 33%, and after 30 min by 22% in relation to the AOC content in the water after the ozonation process. The BDOC content (in relation to raw water) after ozonation and radiation for 10 min increased by 13%, whereas after 30 min no statistically significant changes in the BDOC content were found (Figure 6). Supporting ozonation with UV radiation caused a decrease in BDOC content both after the contact time of 10 min and 30 min (compared to ozonation alone). The BDOC content decreased after 10 min of radiation by 27%, and after 30 min by 31% in relation to the content of BDOC in water after ozonation.

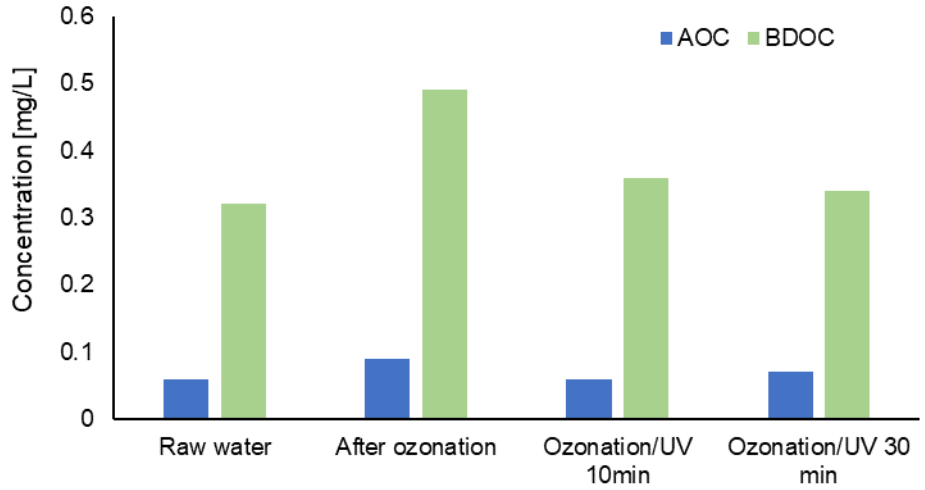

Figure 6. Concentrations of AOC and BDOC in water from the dam reservoir after the ozonation/UV process.

4. Discussion of the Results

In the analyses conducted in this research, it was demonstrated that regardless of the type and origin of water, with an increase in O_3 dose and ozonation time, the content of DOC decreased, while the content of BDOC and AOC increased in each analysed sample. The BDOC increase ranged from 53 to 159% and that of AOC from 40 to 560%. The upward trend of these parameters is consistent with the literature data. Świderska-Bróż and Wolska [25] studied the effectiveness of surface water purification processes in the removal of biodegradable organic substances on a technological scale, where the surface water was oxidised with O_3 (0.8–2.0 gO_3/m^2 for 49.4–72.0 min). The authors showed that O_3 oxidation in all water samples increased the BDOC and AOC content to a level above the limit values characteristic of biologically stable water. Ozonation has been shown to convert refractory components of dissolved organic matter (DOM) into BDOC [26]. The change in BDOC content is influenced by the chemical composition of organic substances, their molecular weight, and the enzymatic activity of bacteria.

The influence of oxidation processes on the change in the forms of organic substances naturally present in water was also studied by Świetlik et al. [27]. The authors demonstrated that the content of BDOC in model water after ozonation increased by 85%, while an increase in this parameter was observed, ranging from 76% (for the lowest dose of O_3 and the lowest contact time) to 200% (for the highest dose of O_3 and highest contact time). After the ozonation of water from plants M, W, L, and R with different doses of O_3, it was observed that the lowest increase in BDOC content (58%) was at the lowest dose of O_3 (1.6 mg/L) and 4 min of contact, and the highest (197%) was at the highest dose of O_3 (10.0 mg/L) and 15 min of contact (Table 2). Similar results were obtained by Raczyk-Stanisławiak et al. [28], who studied the biodegradability of organic DBPs during ozonation in groundwater with a TOC content of 3.8–6.5 mg/L. The authors showed that the amount of biodegradable by-products formed during the oxidation of water with O_3 correlated with the doses of oxidants. After the ozonation of water, an increase in BDOC of 300% was noted. The results obtained indicate that the threshold values of AOC and BDOC in water are related to the O_3 dose. AOC plays a major role in bacterial growth in the presence of a low dose of O_3. Biological stability of water can be guaranteed by O_3 [29].

Pick et al. [30] proposed a new conceptual model to describe and understand the role of AOC within the water supply network that highlights the main role of biofilms in AOC cycling. Other researchers report threshold values for AOC and BDOC in biologically stable water [31]. The drinking water is biologically stable when BDOC is <0.20 mg/L and AOC is 200 μg/L [31,32]. The limit BDOC values in these studies are lower than those reported here, because the limit AOC or BDOC values vary depending on the dose of the disinfectant. The results show that AOC and BDOC contents were different in water from the backyard well and the dam reservoir. This may be due to the content of pollutants in the different sources of water that were the basis for the study. The components of the dam reservoir were more complex than those of the backyard well. Consequently, the AOC or BDOC content for the dam reservoir differed from those for the backyard well.

Thayanukul et al. [33] investigated the ability of secondary bacterial contamination caused by the presence of assimilable organic carbon in various waters. The authors found that the concentration of AOC in the treated water in water treatment plants equipped with the ozonation system was significantly (two to five times) higher, which is confirmed by the results obtained for the tested water samples. The authors suggested that O_3 can break down macromolecules of organic compounds into smaller compounds (carboxylic acids, aldehydes, and ketones), which are more easily absorbed by microorganisms, which is also confirmed by the research of Hammes et al. [34]. After the ozonation of water from the treatment plant with different doses of O_3, it was shown that the lowest increase in AOC content (29%) was at the lowest dose of O_3 (1.6 mg/L) and 4 min of contact, and the highest (400%) was at the highest dose of O_3 (10.0 mg/L) and 15 min of contact (Table 3). This can be explained by the fact that the application of a higher dose of O_3 induces an increase in AOC content and favours bacterial activity. Organic substances present in the water after

the disinfection process are clean, and can transform into AOC and pose uncertainty to the biological stability of the finished drinking water. However, other studies have shown that the organic carbon content of biologically filtered ozonated water was as high as before ozonation [35].

The test results showed that the higher the TOC content in the tested water samples, the higher the AOC content, and the higher the O_3 dose, the more AOC and BDOC are formed. Similar results for AOC were obtained by Polańska et al. [36]. The authors studied the AOC content in tap water in Belgium and showed that ozonation significantly increases the AOC content in water. In addition, they observed that during the ozonation of water, the TOC content affects the formation of AOC, i.e., the higher the TOC content in the water, the more AOC is formed. The increase in the AOC content is also influenced by the increasing dose of O_3. For example, the increase in AOC content in ozonated water with an O_3 concentration of 1 ppm was 1.5 to 4.5 times (i.e., an average of 2.9 times) higher than in non-ozonated water. With an increased concentration of O_3, i.e., 4 ppm, the AOC content increased 10.5 to 12.8 times (i.e., an average of 11.7 times). Ozone resulted in an additional AOC production of an average of 97 mg/L for a 1 ppm O_3 dose, 190 mg/L for an O_3 dose between 2.5 and 3.5 ppm, and 373 mg/L for an O_3 dose of 4 ppm [36]. The upward trend in BDOC content with the increase in the O_3 dose was confirmed by Yavich et al. [37]. The authors analysed the biodegradability of natural organic matter after the ozonation of lake and river waters in the USA. They used three different doses of O_3 for each of the waters: for river water—0.5, 0.75, and 1.0 mgO_3/mgC; and for lake water—0.75, 1.5, and 3.0 mgO_3/mgC. BDOC in raw water from the river was at the level of 1.15 mg/L; after ozonation with the lowest dose of O_3, the content of BDOC increased by 101%, then with the second dose by 121%, and with the highest dose by 142%. The greatest increase obtained by Yavich et al. [37] was similar to the increase in the content of BDOC in water from the Kozłowa Góra reservoir (159%—at the highest dose of O_3 10.0 mg/L and 15 min of contact) (Table 4). In raw water from the lake, the BDOC content amounted to 0.5 mg/L; after ozonation with the lowest dose of O_3, the BDOC content increased by 20%, with the second dose by 36%, and with the highest dose by 48%. In this case, the increase in BDOC content was at the level of 48% and was similar to the increase in BDOC content in water from the Kozłowa Góra reservoir (53%—at the lowest O_3 dose of 1.6 mg/l and 4 min of contact). The upward trend in BDOC content with increasing O_3 dose was not confirmed by the study by Klymenko et al. [38]. The authors applied three doses of O_3: 6, 18, and 60 mgO_3/L. The content of BDOC in water before ozonation was 3.5 mg/L. At the lowest dose, the amount of BDOC increased to 8.8 mg/L; at the dose of 18 and 60 mg/L, it increased to 14.7 mg/L.

For water from the dam reservoir, ozonation assisted by UV radiation resulted in a decrease in AOC content, suggesting that complex transformations occur in the water during this process, in which AOC undergoes a chemical reaction. This results may explain the observed decrease in the AOC content. Microbial cell lysis may also release organic matter into the water, thus increasing O_3 demand [33,39]. AOC and BDOC are not yet monitored as obligatory indicators in the drinking water distribution systems (DWDS). There is a general lack of laws to regulate the AOC and BDOC contents in the treated drinking water before entering DWDS [9]. The main reason can be attributed to the complex nature of AOC, which occurs as a mixture of chemicals, and existing AOC tests are time-consuming and labour-intensive. Therefore, it is desirable to understand the transformation of AOC during disinfection.

In the literature, the biological stability of drinking water is defined differently [1,6]. In order to assess the biological stability of water, different parameters are determined and thus different analytical methods are used. In the case of the AOC and BDOC parameters, there are no standardised value limits for biologically stable water. In addition, there is considerable disagreement about the role of BDOC in assessing the biological stability of drinking water [6]. Oxidation processes, such as chlorination and ozonation commonly used to disinfect water, often result in the modification of the substrate composition. Overall,

oxidative processes create a new niche for bacterial growth, which is not fully explored. These knowledge gaps represent a limitation and challenge to supplement research in this area. The proposed research and results are a partial answer to the problems posed. To date, there has been no study on the effects of different ozonation conditions (i.e., O_3 dose and the time of contact with water) and the combined method (ozonation/UV) on the levels of the biodegradable organic fraction; therefore, this article introduces a new perspective and a new element of knowledge.

The proposed solution will allow the selection of appropriate disinfection methods to prevent the secondary growth of microorganisms in the distribution system. The proposal is part of green environmental technology, which is based on the application of environmental science to protect the environment and resources. Due to increasingly stringent requirements for sustainability and circular economy, the treatment of contaminated water using traditional technologies has often become a formidable challenge. Green technology is also about the sustainable management of raw materials and waste. It aims to provide not only "green" products, but also services. In this context, the results of this research are a proposal for implementing technological innovations. Improving the sustainability of water quantity involves many activities in the areas of innovative water purification methods and implementing opportunities for water recycling, among others [40]. The present research is expected to aid in the selection of appropriate technologies for water disinfection and would lead to an addition in the existing knowledge base on the changes in biodegradable organic substances in drinking water treatment, enabling further research in this domain [2].

5. Conclusions

Based on the obtained test results, it was demonstrated that the concentration and contact time of the selected disinfectant, i.e., O_3, affect the change in the content of AOC and BDOC in water. The hypothesis that the content of biodegradable organic carbon fractions in water during the disinfection process depends on the type of disinfection method used was confirmed by the obtained results. As the O_3 dose and contact time increased, the AOC and BDOC content in the water also increased in direct proportion. The greatest change in AOC and BDOC was observed for groundwater (taken from a well) at an O_3 dose of 10.0 mg/L and a contact time of 15 min, with an increase of 400 and 197%, respectively. Supporting the ozonation process with UV radiation (ozonation/UV) influenced the change in the content of AOC and BDOC; however, the same correlations of changes in the tested waters were not demonstrated. For groundwater, the content of AOC and BDOC after 30 min of UV radiation increased by approximately 67% relative to the content of these parameters in water after the ozonation process. On the other hand, for water taken from the dam reservoir, it was shown that after disinfection with O_3 assisted by UV radiation, the content of AOC and BDOC decreased after both 10 min and 30 min of radiation in relation to water after ozonation. The AOC content decreased by 33% and 22%, respectively, and the BDOC content by 27% and 31%, respectively. The obtained results confirm that it is advisable to expand the range of indicators with BDOC and AOC as routine parameters monitored and measured in purified water. The proposed solution will allow for the selection of appropriate disinfection methods to prevent the secondary growth of microorganisms in the distribution system.

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