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# Changes in selected quality parameters during the treatment and distribution of water

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#### ABSTRACT

The main goal of water treatment plants is water intake from water's natural sources and its preparation for consumers. After the water treatment process, water has to meet requirements of legal standards regarding chemical and microbiological composition. The quality of water from water pipes depends on: its initial composition, the way of treatment, storage, the condition of water system, terminal, and plumbing. The choice of the technological process of water treatment depends on raw water quality, which is often different at the consumer's tap from the one delivered to the distribution system since water undergoes complex physical, chemical, and biological processes. This results in, so-called, secondary water contamination in a distribution system. In this article, the value changes of selected chemical water quality parameters have been presented during both ozone and sodium hypochlorite disinfection. Water samples were collected from underground water intakes. The results showed that disinfection processes did not negatively affect water quality. The number and the extent of changes to the water quality parameters were similar in the case of both ozone and sodium hypochlorite disinfection processes. All examined water samples showed an increase in total hardness following the treatment process and a decrease in the TOC content in water in the distribution process.

*Keywords:* Water disinfection; Quality parameters of water; Water treatment; Ozonation; Chlorination; Chemical oxidation

#### 1. Introduction

The quality of tap water depends on its composition at the intake, treatment and storage methods and the condition of the network, connections and water distribution system. The choice of technological processes for water treatment depends largely on the quality of raw water.

In contrast to surface water, underground water has a rather constant physicochemical composition. In contrast, surface water usually has a high content of substances of different properties, which changes in time, and different susceptibility to removal [1–5].

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In terms of quality, underground water is much better than surface water, which is commonly polluted to a great extent [6–11]. This is due to the constant contact of surface water with water of different origin, for example rainwater and solid and gaseous pollutants [12]. Therefore, the underground water treatment process requires simpler technological processes than surface water.

Over the past 30 years, changes have been made to the intake of water for water distribution system in Poland. The share of surface water intake in the total number of exploited resources declined from 67% in 1980 to 29.6% in 2012, which is 601.4 hm<sup>3</sup>, while the underground water intake increased from 33% in 1980 to 70.4% in the year 2012, which is 1429.5 hm<sup>3</sup> [13].

Due to growing importance of underground water used in the operation of the water distribution system, it is important to monitor underground water quality changes in the process of treatment in Poland. This is necessary because, on the one hand, water is necessary to live, however, it can carry pathogenic microorganisms and toxic substances. It may happen that water after the process of intake, treatment, and distribution does not meet quality requirements [6,7,14–18].

The general pollution of the environment causes deterioration of water quality. Montana [19] gives the information that annually in the world, there are produced 250,000 new compounds, which tend to be well soluble in water. Furthermore, the trade produces 150 million tons of compounds, of which 1/3 is released to the environment, including water [19].

Water treatment plants have to apply the technologies which do not let pollution enter into water pipes. During exploitation, there may appear unfavorable natural conditions (i.e., rain, thaw), which cause surface water runoffs polluted by fertilizers and pesticides. There also appear emergencies (transport accidents, release of untreated sewage), which lead to water pollution by various compounds. Another group is secondary water contamination which occurs on account of stoppage of water supplies, pressure fluctuations in the water pipe network, corrosion of the water system, an application of strong oxidants which can contribute to a formation of by-products of disinfection process [14,16–18].

The issue of water quality is raised not only by monitoring agencies, but also by consumers. It is related to water from collective supply systems (water pipes) and farms which have their own water intakes (wells).

According to the current legal regulations, water should not contain pathogenic microorganisms, parasites and other life forms, pollutants, or substances of natural origin in such an amount that is hazardous to health and adversely affects taste, smell scent, color, and turbidity.

The quality of water delivery for human consumption in Poland is regulated by the Minister of Health Regulation of 29 March 2007 on the quality of water delivery for human consumption (Journal of Laws No. 07.61.417, as amended) [20]. Water delivery for human consumption must meet certain requirements regarding water at the consumer's tap. Therefore, water introduced into the water distribution system must be chemically and biologically stable in order to minimize the danger of secondary water contamination in the distribution system [6]. So far, research carried out in Poland has been focused on the examination of secondary water contamination in terms of its causes, the scale of pollution, and its impact on water quality. Attempts have also been made to prevent pollution. The effectiveness of its removal and the impact of the condition of the water distribution network on its occurrence were assessed [1-7,12,14-19,21-26].

# 2. Materials and methods

#### 2.1. Materials

To conduct the research, water samples were taken from water intake points which include springs and wells for the particular water treatment plants and pumping stations at the treatment point located in the Silesia province, Poland. In the area where the company operates, the water supplied to consumers is underground water only. The selected water supply pipeline covers an area of approximately 1,000 km<sup>2</sup> and delivers water to approximately 328.5 thousand residents. It uses 60 deep wells and 1 spring, grouped into 5 primary and 14 auxiliary intakes, supplying water through a network of water mains and distribution pipelines with a length of 2,308 km. It includes 9 storage tank and 13 hydrophore plants and network pumping stations which form an indivisible water supply system.

The main water network is composed of iron tubes of the diameter larger then  $\emptyset$  250 mm, whereas distribution network is made of gray iron—41%, PVC —37.1%, steel—5.8%, asbestos cement—3.3%, PE—12.5%, spherical iron—0.3%. Connections are made of steel and PE tubes. The total water consumption is 14.328,2 thousand m<sup>3</sup>/y, whereas the average water consumption is 1,213 L/person/d.

Basic operational—technical data of A intake:

 Intake's maximum efficiency is 38,400 m<sup>3</sup>/d. The 2013 A intake analysis showed that the intake's average daily delivery was 19.38 thousand  $m^3/d$ , which made up 40.61% of total water intake in the examined city.

- (2) It is a multiple opening underground intake which began to operate in 1955. It consists of 18 underground wells of the depth of 38–133 m. The intake is from Upper Jurassic aquifer limestone rocks.
- (3) Water treatment: due to high quality water, it is not treated in order to maintain biological stability of water during distribution, water is ozonated, and then pumped into water distribution system using a four pump.
- (4) The most adverse impact on the water quality in A intake wells is exerted by industrial pollutants that enter the wells from industrial areas south of the intake. A nearby steelworks used to be the source of chemical pollution. Water was also contaminated due to limestone quarrying. This led to the emergence of numerous pits, which are, unfortunately, frequently used as sewage and waste disposal sites.

Basic operational—technical data of B intake:

- (1) Intake's maximum efficiency is  $29,800 \text{ m}^3/\text{d}$ ,
- (2) It consists of 5 underground wells of the depth of 42–71 m. The intake is from Upper Jurassic aquifer limestone rocks. It is the oldest underground water intake which began to operate in 1955.
- (3) Water treatment: In order to pump raw water from well openings, underwater pumps are used. Next, water is delivered to the pump station and treatment plant area, where the spring is located, through pipeline. Two pumps are used to transport water from the source. Then, all water (from the well and the spring) is divided into two streams. A part of water (approximately 50%) is delivered to the nitrate removal plant, while the rest is delivered directly to the ozone treatment plant. A process of biological denitrification occurs in the water delivered to the treatment plant. The used technology facilitates the reduction of 80-82% of nitrates. Then, water is delivered to the contact tank of the treatment plant, where it undergoes ozone treatment together with raw water delivered directly from the well and spring. Finally, water is delivered to the water distribution network by 4 pumps.

The main threat to water quality is a high content of nitrates coming from untreated communal wastewater released directly to the ground or leaking wastewater tanks as well as from unmonitored communal waste landfills, which results from a significant delay of the sewage system installation in comparison with the water distribution system in the area of the flow of underground water to B intake.

Basic operational—technical data of C intake:

- (1) Intake's maximum efficiency is  $19,680 \text{ m}^3/\text{d}$ ,
- (2) It consists of 5 underground wells of the depth of 69–72 m. The intake is from Upper Jurassic aquifer limestone rocks, which began to operate in 1974.
- (3) Water treatment: due to its high quality, water is not treated in order to maintain biological stability of water during distribution. Water is chlorated and then pumped into the water distribution system using a three-pump system.
- (4) due to low level of aquifer isolation in the form of poorly permeable rock cap (approximately 50%), this underground water reservoir is continuously at risk of surface pollution inflow. The main source of water and ground nitrate compound pollution in the area is untreated communal wastewater released directly to the ground or from leaking wastewater tanks as well as from unmonitored communal waste landfills, which results from a significant delay of sewage system installation in comparison with water distribution system. Moreover, the presence of nitrates in water is connected with the communal disposal of wastewater and sludge, solid waste (unmonitored waste landfills), and farming (liquid manure, fertilizers).

Basic operational-technical data of D intake:

- (1) auxiliary intake of the examined city.
- (2) the intake is from Triassic aquifer (limestone, dolomite). There is 1 underground well (460 m).

The process of water treatment consists of the following stages:

- water intake and delivery from the underground well to the water treatment plant;
- (2) aeration of water (oxidation of iron compounds present in raw water);
- (3) de-ironing; disinfection by sodium hypochlorite solution and delivery of treated water to distribution system by pumps.

The research also included the analysis of water samples taken from faucets at the consumers. The samples were collected in accordance with the standards set by the Polish Committee for Standardization [27]. Water from the intake stations marked A and B symbols was treated with ozone, while water from the intake stations C and D was treated using of sodium hypochlorite.

# 2.2. Analytical procedure

Water samples were collected for examination in the morning, around 8 (after the night stagnation, at a time of high water consumption). The samples underwent a physicochemical analysis. The following physicochemical indicators were determined: turbidity, color, odor, pH, ammonium ion, nitrite, nitrate, permanganate index, chlorides, total iron, total hardness, alkalinity, non-carbonate hardness, free carbon dioxide, dissolved oxygen, electrical conductivity, residual ozone total organic carbon (TOC), manganese, sulfates, calcium, magnesium, fluoride, phenols (phenol index), free chlorine, phosphates.

Changes in physicochemical composition of water in the distribution system were determined by means of comparing quality indicator values of water samples collected from faucets at consumer's tap with the quality of water entering the network and the quality of raw water. In order to assess changes in water quality, selected physicochemical water quality indicators were identified in accordance with the applicable standards of the Polish Committee for Standardization [28].

### 3. Results and discussion

Raw water from the intake A, which is taken from several wells, is stored in two tanks: left and right. The values of parameters in Table 1 are average values of water parameters from both tanks, left and right. Then, the water undergoes ozonation in the treatment plant, and next, it is pumped to the water supply network in the pumping station.

The analysis of the selected changes of the physicochemical quality parameters of water, which was taken from the intake station A (Table 1), showed that the parameters, which values changed to the greatest extent in the distribution process (pumping station consumer), include: smell, nitrate content, chloride content, content, and non-carbon hardness. The values of the following indicators increased: nitrates by 64.4%, non-carbonate hardness by 43.0%, chlorides by 29.0%. It was noticed that general iron was present in consumer water. Turbidity in consumer water was 0.69 NTU, whereas in other water samples, it was below detection limit. Both electrical conductivity and total hardness increased to a lesser extent by 13.0% and 3.9%, respectively. The values of alkalinity, dissolved oxygen, free carbon dioxide, and TOC decreased. The alkalinity value decreased by 11.5%, free carbon dioxide by 12.5%, dissolved oxygen by 13.2%, TOC by 2.2%. The ozone content in the water from the pumping station was 0.040 mg/L, whereas in consumer water, its content was below detection limit. The values of other indicators did not change.

The analysis of the changes of the physicochemical quality parameters of water A in the process of water disinfection (raw water-pumping station water) showed that smell (from the very weak plant smell to the specific ozone smell in the 3rd degree) is a parameter whose values changed the most in the water treatment process (Table 1). In addition, the values of both TOC and dissolved oxygen rose significantly by 23.0% and 28.2%, respectively. Alkalinity increased by 1.0%, nitrates content by 2.3%, total hardness by 2.0%, chlorides content by 4.8%, non-carbonate hardness by 5.2%, and free carbon dioxide by 14.3%. Turbidity in the right tank was 0.31 NTU, but in the left tank and in pumping station water, it was below detection limit. The water sample collected at the pumping station indicated the presence of ozone residue. The values of the other indicators did not change during the water treatment process.

Raw water (intake B) is taken from the spring and the well no. 3. The values of parameters in Table 2 are average values of water parameters from the spring and well no. 3. Then, the water undergoes ozonation in the treatment plant, and next, it is pumped to the water supply network in the pumping station.

The values of the physicochemical parameters of water quality delivered into the water system were in consonance with requirements set for water is delivered for human consumption, except for the excessive nitrates content in water from the intake station B, which was 62.1 mg/L and exceeded acceptable concentration by 24% [20].

The analysis of the changes of the physicochemical quality parameters of water taken from the intake station B (Table 2) showed that the parameters of water in its distribution did not change much. Smell has changed from the specific ozone scent in the 3rd degree to the very weak plant scent). The values of: the nitrate content, the chloride content, the general hardness, the non-carbonate hardness, and the electrical conductivity rose marginally. Turbidity in consumer water was 0.34 NTU, whereas in other water samples, it was below detection limit. The nitrate content increased to the greatest extent by 12.1%.

Table 1

The '	profile of raw	water a	uality, th	e water	from the	e water	treatment	plant.	and	water	distribution	system	(A)
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Indicator	Raw water	Pump station	Consume
Turbidity, NTU	0.30	<0.30	0.69
Color, mg/Pt	<5	<5	<5
Smell	z1R	z3S(O <sub>3</sub> )	z1R
pH	7.75	7.7	7.7
Ammonium ion, mg/L	< 0.05	< 0.05	< 0.05
Nitrites, mg/L	< 0.018	< 0.018	< 0.018
Nitrates, mg/L	17.6	18	29.6
Permanganate index, mg/L	< 0.50	<0.50	< 0.50
Chlorides, mg/L	17.75	18.6	24.0
General iron, µg/L	<40	<40	76
General hardness, mval/L	3.57	3.64	3.78
Alkalinity, mval/L	2.60	2.62	2.32
Non-carbonate hardness, mval/L	0.97	1.02	1.46
Free carbon dioxide, mg/L	7.7	8.8	7.7
Dissolved oxygen, mg/L	8.58	11.0	9.55
Electrical conductivity at 25 °C, µS/cm	383.5	385	435
Residual ozone, mg/L	_	0.040	< 0.007
TOC, mg/L	0.735	0.91	0.89

Table 2

The profile of raw water quality, the water from the water treatment plant, and water distribution system (B)

Indicator	Raw water	Pump station	Consumer	
Turbidity, NTU	<0.30	<0.30	0.34	
Color, mg/Pt	<5	<5	<5	
Scent	z1R	z3S(O <sub>3</sub> )	z1R	
pH	7.75	7.7	7.7	
Ammonium ion, mg/L	< 0.05	< 0.05	< 0.05	
Nitrites, mg/L	< 0.018	< 0.018	< 0.018	
Nitrates, mg/L	55.7	38.1	42.7	
Permanganate index, mg/L	<0.50	<0.50	< 0.50	
Chlorides, mg/L	28.4	29.5	30.7	
General iron, µg/L	<40	<40	<40	
General hardness, mval/L	4.20	4.12	4.20	
Alkalinity, mval/L	2.01	2.08	2.08	
Non-carbonate hardness, mval/L	2.09	2.04	2.12	
Free carbon dioxide, mg/L	5.5	6.6	6.6	
Dissolved oxygen, mg/L	8.12	9.38	8.94	
Electrical conductivity in 25 °C	472,5	472	476	
Residual ozone, mg/L	_	0.030	< 0.007	
TOC, mg/L	1.02	0.94	0.86	

electrical conductivity value increased by 1.0%, total hardness by 1.9%, chlorides by 4.1%, non-carbonate hardness by about 3.9%. The amount of TOC decreased by 8.5% and dissolved oxygen decreased, respectively, by 4.7%. The ozone content in water from the pumping station was 0.030 mg/L, whereas in consumer water, its content was below detection limit. The values of other indicators did not change.

The analysis of the changes of the physicochemical quality markers of water taken from the intake station B showed that smell (from very weak plant to the specific ozone smell in the 3rd degree) is a parameter whose values changed the most in the water treatment process (Table 2). The content of both dissolved oxygen and the free carbon dioxide increased by 15.6% and 20.0%, respectively. The values of chlorides

content and alkalinity increased by more than 3%. In contrast, non-carbonate hardness decreased by 2.4%, TOC by 7.4%. The largest decrease, however, was shown for nitrates, the content of which decreased by 31.6%.

Residual ozone appeared in the water which was taken from a pumping station. The values of the other parameters did not change significantly during the water treatment process.

Raw water (intake C) is taken from the well no. 10. Then, it undergoes ozonation in the treatment plant, and next, it is pumped to the water supply network in the pumping station.

The analysis of the changes of the physicochemical quality parameters of water taken from the intake station C (Table 3) showed that the content of general iron and turbidity is the parameter whose value changed the most in a distribution process. The turbidity value in consumer water was 1.5 NTU, whereas in other water samples, it was below detection limit. The total iron content was 106  $\mu$ g/L in consumer water, whereas in other water samples, it was below detection limit. The pH and total hardness value increased by 2.6%, alkalinity by 12.2%, and free carbon dioxide by 12.9%. The values of nitrates content, chlorides

content, non-carbonate hardness, dissolved oxygen, free chlorine, and TOC decreased in the examined water samples. The nitrates content by 12.9%, dissolved oxygen by 9.9%, chlorides content by 8.6%, TOC by 7.7%, and non-carbonate hardness by 7.4% decreased. The values of other indicators did not change. Scent has changed as well, from a specific chlorine scent in the 3rd degree to a very weak plant scent. Free chlorine (0.13 mg/L) was detected in pumping station water, while the content of free chlorine in consumer water was below detection limit.

The analysis of the changes of the physicochemical quality parameters of water taken from the intake station C showed that smell (from the very weak plant smell to the specific chlorine smell in the 3rd degree) is a parameter whose values changed the most in the water disinfection process, as well as the content of sulfates, calcium, and magnesium. The abovementioned indicators (Table 3) were not present in water C after disinfection process. A significant change in the dissolved oxygen content was discovered, which increased by 31.3%, while the nitrate content in the examined water increased by 2.7%. The presence of free chlorine was discovered in pumping station water (0.13 mg/L). The values of chlorides

Table 3

The profile of raw water quality, the water from the water treatment plant, and water distribution system (C)

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Indicator	Well no. 10	Pump station	Consumer
Turbidity, NTU	<0.30	< 0.30	1.5
Color, mg/Pt	<5	<5	<5
Smell	z1R	z3S(Cl <sub>2</sub> )	z1R
pH	7.7	7.7	7.9
Ammonium ion, mg/L	< 0.05	< 0.05	< 0.05
Nitrites, mg/L	< 0.018	< 0.018	< 0.018
Nitrates, mg/L	48.3	49.6	43.2
Permanganate index, mg/L	< 0.50	<0.50	< 0.50
Chlorides, mg/L	25.0	23.3	21.3
General iron, µg/L	<40	<40	106
Manganese—AAS method, $\mu g/L$	<10	-	-
Sulfates, mg/L	49.0	-	-
General hardness, mval/L	4.54	4.20	4.34
Alkalinity, mval/L	2.64	2.30	2.58
Non-carbonate hardness, mval/L	1.90	1.90	1.76
Calcium, mg/L	87.0	_	-
Magnesium, mg/L	2.43	_	-
Free carbon dioxide, mg/L	7.6	6.2	7.0
Dissolved oxygen, mg/L	6.23	8.18	7.37
Fluoride, mg/L	<0.20	-	-
Phenols (phenolic index), mg/L	< 0.001	_	-
Electrical conductivity at 25 °C, µS/cm	497	459	459
Free chlorine, mg/L	-	0.13	< 0.02
TOC, mg/L	1.78	1.17	1.08

content, total hardness, alkalinity, free carbon dioxide, electrical conductivity, and TOC decreased. The largest change occurred for TOC, the amount of which decreased by 34.3%; the content of chloride, total hardness, and electrical conductivity decreased by 6.8, 7.5, and 7.7% respectively, alkalinity by 12.9%, and free carbon dioxide by 18.4%. The values of the other parameters did not change significantly during the water treatment process.

Raw water (intake D) is taken from the spring. Then, it undergoes ozonation in the treatment plant, and next, it is pumped to the water supply network in the pumping station.

The analysis of changes in quality indicators of water taken from intake D (Table 4) showed that the parameters whose values changed in the distribution process to the greatest extent included: manganese, sulfates, calcium, magnesium, and fluorides, which were not found in the water collected from the consumer. Non-carbonate hardness value changed to a great extent in the examined water—by 50.0%, the chloride content increased by 15.7%, nitrates by 14.3%, electrical conductivity by 6.6%, and total hardness by 3.4%. The values of turbidity, alkalinity, free carbon dioxide, dissolved oxygen, and TOC decreased. The

largest decrease was reported for turbidity and free carbon dioxide, which decreased by 25.5%, dissolved oxygen by 22.8%, alkalinity by 3%, and TOC by 2%. In consumer water, color has changed to the value of 5 mg/Pt. The free chorine content decreased from the value of 0.03 mg/L to below detection limit. The values of other indicators did not change.

The analysis of the changes of the physicochemical quality parameters of water taken from the intake station D showed the parameters which changed significantly included smell (from the specific smell of hydrogen sulfide in the 3rd degree to very weak plant smell), the phosphates content, which were not found in water after the treatment process (Table 4). The content of magnesium decreased significantly (by 93.1%), non-carbonate hardness by 39.4%, turbidity by 37.8%, manganese by 25.5%, fluorides content by 22.7%, sulfates by 20.4%, chlorides by 13.6%, electrical conductivity by 9.3%, total hardness by 6.8%, and calcium content by 6.3%. General iron content fell from 230 µg/L to the value below detection limit. Similarly, color decreased from 5 mg/Pt to the value below detection limit. The examination of the water revealed a significant increase in dissolved oxygen (by 146.0%). The nitrate content and TOC also increased by 21.7%

Table 4

The profile of raw water quality, the water from the water treatment plant, and water distribution system (D)

Indicator	Well	Pump station	Consumer
Turbidity, NTU	0.82	0.51	0.38
Color, mg/Pt	5	<5	5
Smell	z3S(H <sub>2</sub> S)	z1R	z1R
pH	7.8	7.9	7.8
Ammonium ion, mg/L	< 0.15	< 0.05	< 0.05
Nitrites, mg/L	<0.018	< 0.018	< 0.018
Nitrates, mg/L	0.46	0.56	0.64
Permanganate index, mg/L	< 0.50	< 0.50	< 0.50
Chlorides, mg/L	11.8	10.2	11.8
General iron, µg/L	230	<40	<40
Manganese—AAS method, µg/L	55	41	_
Sulfates, mg/L	47.0	37.4	_
General hardness, mval/L	3.84	3.58	3.70
Alkalinity, mval/L	3.18	3.18	3.10
Non-carbonate hardness, mval/L	0.66	0.40	0.60
Calcium, mg/L	50.5	47.3	-
Magnesium, mg/L	216.0	14.8	-
Phosphates, mg/L	0.178	_	-
Free carbon dioxide, mg/L	8.8	8.8	6.6
Dissolved oxygen, mg/L	2.55	6.28	4.85
Fluoride, mg/L	0.66	0.51	_
Phenols (phenolic index), mg/L	< 0.001	_	_
Electrical conductivity at 25 °C, µS/cm	432	392	418
Free chlorine, mg/L	-	0.03	< 0.02
TOC, mg/L	1.16	1.30	1.28

and 12.1%, respectively. The presence of free chlorine was discovered in the water collected from the pumping station. The values of the other parameters did not change significantly during the water treatment process.

After the water treatment process, residual ozone appeared in water A and B. It is due to application of ozone as a disinfectant. By contrast, after the water treatment process, free chlorine appeared in water from C and D intake stations. It is caused by application of sodium hypochlorite as a disinfectant.

During the raw water treatment process, water is oxygenated, which was the cause of an increase in the amount of dissolved oxygen in all water samples collected at the pumping station.

The changes of the physicochemical quality parameters of water largely depend on a method of the water treatment process and on a characteristics of raw water [7,15].

The comparison of the research results of water samples collected at the pumping station and at the consumer's tap revealed the following similarities:

- (1) in the case of ozonated water A and B, an increase in the value of: turbidity, the nitrate content, the chloride content, general and noncarbonate hardness, electrical conductivity and a decrease in the values of: TOC, dissolved oxygen, and ozone were observed.
- (2) in the case of chlorinated water C and D, an increase in the value of total hardness, and a decrease in the value of the following indicators: dissolved oxygen, free chlorine, and TOC were observed.

The comparison of the research results of the raw water and the water from the pumping station revealed as follows:

- (1) in the case of ozonated water A and B, the content of dissolved oxygen, chlorides, free carbon dioxide, and alkalinity increased.
- (2) in the case of chlorinated water C and D, the content of nitrates and dissolved oxygen increased;
- (3) in the case of chlorinated water C and D, general hardness, the content of chlorides, sulfates, calcium, magnesium, and electrical conductivity decreased.

It was also discovered that there was a change in smell for samples A and B in the line raw water pumping station: from very weak plant smell to specific grade 3 ozone smell and for samples A and B in the line pumping station—the consumer: from the specific grade 3 ozone smell to very weak plant smell, which resulted from changes in the amount of ozone in water at various stages of the water treatment process.

The common features of the water samples from A, B, C, and D intakes in the line pumping station the consumer included an increase in total hardness and nitrate content (with the exception of water C, in which case the value decreased by 14%) and a decrease in dissolved oxygen and TOC content. However, the research of samples in the line raw water—the pumping station revealed that in the case of ozonated water, the content of chloride and total hardness increased, while in the case of chlorinated water, the values of these indicators decreased.

The obtained results show that in each examined sample, the content of TOC in water decreased in the line pumping station-consumer. The reduction of the TOC amount during the treatment processes has been confirmed in the literature [29,30]. The decrease in the TOC content in water during the process of oxidation using chlorine was proven by Swiderska-Broz and Wolska [29,31]. The authors also indicated that the amount of ammonium nitrogen in water decreased during the chlorine oxidation process, which is confirmed by the results obtained for water from intake D. According to Kowal, the TOC content in purified water decreased by 9.1% in the case of underground water relative to the content in raw water and after chlorination to 12.1% relative to raw water [7]. According to Kowal [7], Swiderska-Broz and Wolska [32], the reduction of the TOC content in the water distribution system may result from both precipitation and settling of organic chemicals in the pores of the inner walls of water pipes. According to other literature sources, the cause of a decrease in the TOC content is that these substances are used as a source of carbon and energy in microbial development and growth in water [21-23,33,34]. Raczyk-Stanislawiak et al. emphasize that oxidants used in water treatment are very reactive and, therefore, strongly process organic substances contained in water.

In 3 of 4 examined water samples, there was an increase in the nitrate content in the line pumping station—consumer, which may indicate the, so-called, secondary water contamination [2–5,8–11,15–18,25,31] and the presence of nitrifying bacteria in the distribution system [7].

Changes in the value of water quality indicators of the examined water can be caused by chemical reactions between the substances present in water during its distribution [15], chemical reactions between disinfectants used and the substances found in raw water and the, so-called, secondary water contamination, which has been confirmed in the literature [2–5,7–11,15–18,24].

A decrease in the content of free chlorine in the line pumping station–consumer was caused by the fact that chlorine was used in chlorination and oxidation reactions occurring during distribution of water in pipelines as well as reactions on the surface of pipelines [35].

There was an increase in the overall iron content in the water A and C in the process of distribution, which contributed to an increase in turbidity. The same relationship was described by Nowacka et al.[30], who connected that increase in turbidity with the high content of iron ions. This relationship has also been demonstrated by Kowal in his research [7].

In the case of ozonated water, the chloride content increased in water samples in the line raw water pumping station, while in the case of chlorinated water, this value decreased. A similar problem was described by [23,26,33,36–39] who claimed that its cause was the fact that the ozonation of water leads to a greater amount of, so-called, water disinfection byproducts (DBPs), including chlorides. The largest amount of DBPs is formed through ozonation, a smaller amount when using a chlorine dioxide and the smallest as a result of Cl<sub>2</sub> chlorination.

#### 4. Summary and conclusions

A water distribution system is a complex reactor in which physical, chemical, and biological processes can occur changing a physicochemical and bacteriological composition of water. There are many reasons of the secondary water contamination. The authors [2-5,8-11,15–18,31,32] give the information that the main reasons regarding the changes of values of water quality parameters include: the changes of chemical and biological stability of water which is delivered into the water system, insufficient quantity of disinfectant in water in the whole distribution system, inappropriate, and changeable hydraulic conditions which prevail during water delivery to its consumers, the properties of installation materials, technical, and sanitary condition of all the elements of the distribution system along with the changes which occur in it. Due to complexity of the problem, it is hard to unequivocally define the function of particular factors which affect water and its quality in the treatment and distribution processes. Moreover, these factors usually lead to secondary water contamination collectively.

The research led to the following conclusions:

- (1) water collected from the examined intakes was chemically stable,
- ozonation and chlorination of the examined water and its distribution did not negatively affect water quality,
- (3) a feature common to all examined water samples was an increase in total hardness following the treatment process and a decrease in the TOC content in water during the distribution process,
- (4) the number and degree of changes to the values of quality parameters were similar in the disinfection process using both ozone and sodium hypochlorite,
- (5) in the case of ozonated water in the process of water distribution, the values of twice as many water quality parameters changed as it was in the case of chlorinated water.

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## References

- M. Swiderska-Broz, M. Wolska, Efficiency of surface water treatment processes at removing biodegradable organic substances, Ochrona Środowiska 33 (2011) 77–80. (in Polish).
- [2] I. Zimoch, A. Stolarczyk, Raman spectroscopy in estimating THM formation potential in water pipe network, Environ. Protect. Eng. 36 (2010) 55–64.
- [3] I. Zimoch, Assessing spatial variations of water quality in water-pipe network by analysis of THM formation, Ochrona Srodowiska 29 (2007) 49–52. (in Polish).
- [4] M. Kucharski, Analyzing the changes in the quantity of ozonation and chlorination by-products in tap water for City of Bialystok, Ochrona Środowiska 33 (2011) 46–51. (in Polish).
- [5] I. Zimoch, Modeling of trihalomethanes concentrations in tap water, Ochrona Środowiska 33 (2011) 35–42. (in Polish).
- [6] M. Pawlaczyk-Szpilowa, Sanitary quality on drinking water, Ochrona Środowiska 3 (1993) 12–15. (in Polish).
- [7] A. Kowal, Water quality variations in distribution system and relevant preventive measures, Ochrona Środowiska 25 (2003) 3–6. (in Polish).
- [8] M. Łebkowska, Antibiotic resistant bacteria in drinking water, Ochrona Środowiska 31 (2009) 11–15. (in Polish).
- [9] I. Zimoch, A. Szostak, Assessing the efficiency of water treatment involving active carbon in water treatment plant Goczałkowice, Ochrona Środowiska 27 (2005) 17–20. (in Polish).

- [10] R. Korol, A. Bozek, U. Szyjkowska, M. Strońska, Quality of surface water used for drinking water recovery, Ochrona Środowiska 25 (2003) 17–22. (in Polish).
- [11] W. Balcerzak, I. Zimoch, Mathematical modeling of water quality variations i Dobczyce Reservoir, Ochrona Środowiska 19 (1997) 69–72. (in Polish).
- [12] M. Swiderska-Broz, Some major problems faced in water treatment for drinking purposed, Ochrona Środowiska 3 (1999) 7–12. (in Polish).
- [13] Information & Works of Central Statistical Office of Poland, Environment Protection, Warsaw (2012) 105–108.
- [14] A. Wojas, M. Dabek, G. Piotrowska, Water quality from an intake to the dispenser, Environ. Eng. 20 (2008) 42–49. (in Polish).
- [15] M. Swiderska-Broz, M. Wolska, Major contributors of self-contamination of water in distribution system, Ochrona Środowiska 28 (2006) 29–33. (in Polish).
- [16] I. Zimoch, E. Łobos, The optimization of chlorine dose in water treatment process in order to reduce the formation of disinfection by-products, Desal. Wat. Treat. 52 (2014) 1–6.
- [17] M. Domanska, J. Lomotowski, Rate of chlorine and chlorine dioxide decay in the water-pipe network, Ochrona Środowiska 31 (2009) 47–49. (in Polish).
- [18] I. Zimoch, Operational safety of the water supply system under conditions of water quality variations in the water-pipe network, Ochrona Srodowiska 31 (2009) 51–55, (in Polish).
- [19] B. Montana, Why Only Reverse Osmosis?, Hydropure Publishing House, Wroclaw, 2006. (in Polish).
- [20] The Minister of Health Regulation of 29 March 2007 on the quality of water delivered for human consumption (J. Laws no. 07.61.417, as amended)
- [21] J. Swietlik, U. Raczyk-Stanislawiak, J. Nawrocki, Effect of pre-oxidation followed by biodegradation on a molecular weigh distribution of natural organic matter, Ochrona Środowiska 27 (2005) 27–32. (in Polish).
- [22] U. Raczyk-Stanislawiak, E. Ciemniecka, J. Swietlik, J. Nawrocki, Removal of precursors of biodegradable organic substances via biofiltration, Ochrona Srodowiska 29 (2007) 59–64. (in Polish).
- [23] E. Zbiec, J.R. Dojlido, By-products of water disinfection, Ochrona Środowiska 3 (1999) 37–44. (in Polish).
- [24] J. Wasowski, A. Grabinska-Loniewska, Recontamination of water in the municipal supply system of the City of Warsaw, Ochrona Środowiska 58 (1995) 60–62. (in Polish).
- [25] Z. Grabowski, B. Rzerzycha, H. Grabowska, M. Wybor, J. Cyran, J. Solnica, Preoxidation of water pollutants with chlorine dioxide and removal of oxidation by-products in Sulejow—Lodz Waterworks, Ochrona Środowiska 3 (2001) 45–48. (in Polish).
- [26] J. Swietlik, A. Dabrowska, U. Raczyk-Stanisławiak, J. Nawrocki, Reactivity of natural organic matter fractions with chlorine dioxide and ozone, Water Research 38 (2004) 547–558.
- [27] Polish Standards and Polish Standardization Documents:PN-ISO 5667-5:2003, Water quality – Sampling – Part 5: Guidance on sampling of drinking water and water used for food and beverage production.
- [28] Polish Standards and Polish Standardization Documents: Turbidity: PN-EN ISO 7027:2003 point 6,

Water quality - Determination of turbidity. Color: PN-EN ISO 7887:2002 ch. 4, Water guality - Examination and determination of color, Smell: PN-C-04557:1972, Water and wastewater - Determination of smell, taste and aftertaste, pH: PB-124 first ed. of 03.02.2012, The own research procedure, potentiometric method, Ammonium ion: PN-C-04576-4:1994, Water and wastewater - Examination of nitrogen compound content determination of ammonium nitrogen in water by means of direct nesslerisation method, Nitrites: PN-EN 26777:1999, Water quality - Determination of nitrite - Absorption molecular spectrometry method, Nitrates: PB-128 first ed., 20.02.2013, The own research procedure, Spectrophotometric method, Permanganate index: PN-EN ISO 8467:2001, Water quality - Determination of permanganate index, Chlorides: PN-ISO 9297:1994, Water quality - Determination of chloride -Silver nitrate titration method in the presence of chromate indicator (Mohr's method), General iron: PB-53 first ed., 21.02.2005, The own research procedure, Spectrophotometric method, General hardness: PN-ISO 6059:1999, Water quality - Determination of total content of calcium and magnesium – EDTA titration method, Alkalinity: PN-EN ISO 9963-1:2001 + Ap1:2004, Water quality - Determination of alkalinity - Part 1: Determination of total alkalinity and alkalinity to phenolphthalein, Non-carbonate hardness: PB-104 first ed., 22.03.2007, The own research procedure, Alkalinity Alkaline (calculations), Free carbon dioxide: PN-C-04547-01:1974, Water and wastewater -Carbon dioxide content examination - Determination of free carbon dioxide in water, Dissolved oxygen: PN-EN ISO 5814:2013-04, Water quality - Determination of dissolved oxygen - electrochemical sensor method, Electrical conductivity in 25°C: PN-EN 27888:1999, Water quality - Determination of electrical conductivity, Residual ozone: PB-120 first ed., 01.12.2010, The own research procedure, TOC: PN-EN 1484:1999, Water analysis - Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC), Manganese - AAS method: PB-122, first ed., 13.09.2011, The own research procedure, Sulphates: PB-41 2nd ed., 22.12.2011, The own research procedure, titration method, Calcium: PN-ISO 6058:1999, Water quality - Determination of calcium content - EDTA titration method, Magnesium: PN-C- 04554-4:1999, Water and wastewater -Hardness examination - Determination of total content of calcium and magnesium in wastewater by titration with EDTA method and the calculation of magnesium content in water and wastewater, Phosphates: PB-105 2nd ed., 29.11.2010, The own research procedure, Spectrophotometric method, Fluoride: PB-121 first ed., 01.12.2010, The own research procedure, Spectrophotometric method, Phenols (phenolic index): PN-ISO 6439:1994 B method, Water quality -Determination of phenol index - Spectrometric Methods of 4-aminoantipyrine after distillation, Free chlorine: PB-101 first ed., 5.02.2007, The own research procedure.

[29] M. Swiderska-Broz, M. Wolska, Changes of organic substances concentration in water during chemical oxidation, Environ. Eng. Prot. 14 (2011) 111–120. (in Polish).

- [30] A. Nowacka, M. Wlodarczyk-Makula, E. Sperczynska, A. Turek, Changes in concentration of total organic carbon in water during treatment processes, Water Technol. 1 (2013) 14–23. (in Polish).
- [31] M. Swiderska-Broz, M. Wolska, Recontamination of chemically ustable water in distribution system, Ochrona Srodowiska 4 (2005) 35–38. (in Polish).
- [32] M. Swiderska-Broz, Contributory factors in the potential of biofilm formation and growth in water distribution system, Ochrona Środowiska 32 (2010) 7–13. (in Polish).
- [33] M. Boualam, L. Mathieu, S. Fass, J. Cavard, D. Gatel, Relationship between coliform culturability and organic matter in low nutritive waters, Water Res. 36 (2002) 2618–2626.
- [34] J.P. Chandy, M.L. Angles, Determination of nutrients limiting biofilm formation and the subsequent impact on disinfectant decay, Water Res. 35 (2001) 2677–2682.

- [35] M. Swiderska-Broz, M. Wolska, Causes underlying free chlorine decay in the water distribution system, Ochrona Środowiska 29 (2007) 19–24. (in Polish).
- [36] U. Raczyk-Stanislawiak, J. Swietlik, J. Nawrocki, Effect of chlorine, chlorine dioxide and ozone on a biological stability of water, Ochrona Środowiska 27 (2005) 33–39. (in Polish).
- [37] W.-J. Huang, G.-Ch. Fang, Ch.-Ch. Wang, The determination and fate of disinfection by-products from ozonation of polluted raw water, Sci. Total Environ. 345 (2005) 261–272.
- [38] C.I. Escobar, A. Randall, A. Taylor, Bacterial growth in distribution systems: Effect of assimilable organic carbon and biodegradable dissolved organic carbon, Environ. Sci. Technol. 35 (2001) 3442–3447.
- [39] K.K. Jyoti, A.B. Pandit, Ozone and cavitation for water disinfection, Biochem. Eng. J. 18 (2004) 9–19.