CHANGES IN THE CONTENT OF BIODEGRADABLE ORGANIC MATTER IN TAP WATER IN THE CITY OF CZĘSTOCHOWA

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Abstract
This paper presents research aimed at the assessment of biodegradable organic carbon content changes (BDOC) during water disinfection process. The water samples examined in the research came from intakes, pumping stations at treatment plants situated in the Silesia district and water consumers. The examined water was underground water. One water sample was disinfected by sodium sub chloride while the other one by ozone. BDOC was determined using the Joret method, which involves observation of dissolved organic carbon (DOC) decrease in the examined water. The research has shown that BDOC content fluctuates at every stage of the treatment process and distribution of the examined water. Another analyzed parameter was biological stability of water.

Keywords: biodegradable dissolved organic carbon, underground water, disinfection, water quality

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 the water distribution system [5]. Water quality introduced into the system co-determines the phenomena which occur in it as well as processes whose products are most often the cause of secondary pollution of water supplied to consumers. To

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minimize adverse changes in the physico-chemical and bacteriological composition of water, it is necessary to ensure its biostability [9]. Biological stability of water means the lack of tendency to stimulate the secondary development of microorganisms in tap water. The absence of water biostability results primarily in the formation and development of biofilm, the increased use of disinfectants, intensification of electrochemical corrosion of metals and dissolution of its products, contributing to secondary water pollution [8]. Water is biologically stable if it is not conducive to microbial growth and is therefore devoid of inorganic and organic nutritious substrates [9].

According to Bonalam et al. and Chandy & Angels, organic carbon has the greatest impact on the development of biofilm forming in water supply network [1, 2]. In contrast to surface water, underground water has a rather constant physicochemical composition. However, surface water usually has a high content of substances of different properties, which changes in time, and different susceptibility to removal [10]. Although underground water is much better than surface water in terms of quality, it is necessary to monitor the water’s quality constantly as it may decline due to many reasons during the exploitation of intakes. The importance of this is emphasized by the fact that there have been changes in water’s intake over the past 30 years in Poland. The changes involved the increase of share of underground water in the total amount of used water resources by 70.4% to 2012. Drinking water is mainly delivered to consumers by water companies, whose duties involve drawing water from natural sources and preparing it in such a way so that it is harmless to consumers. The selection of water treatment technological processes is mainly determined by raw water quality [3].

According Volk & LeChevallier, microorganisms can grow in water containing only trace amounts of nutrient substrates [12]. The organic matter content in water may be the source of carbon and energy for the growth and development of bacteria, which causes the emergence and growth of biofouling in a water distribution system. Disinfectants applied in order to destroy bacteria or prevent their development affect both microorganisms as well as chemical substances present in water, which increases their biodegradability. This leads to biofouling development in a water distribution system and degrades water quality and the condition of the water distribution system [5, 6, 8-11].

According to literature sources, the condition of water biostability is: 150-200 mg C/m³ [3]. On the other hand, Volk et al. (1994) determined a biodegradable organic carbon content changes (BDOC) value of 0.15 mg/L at 20°C and 0.30 mg/L at 15°C for biostability [13]. The indicators illustrate the susceptibility of
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water on secondary pollution by means of available forms of organic carbon. Particular attention is paid to the contents of BDOC and assimilated organic carbon (AOC) [6].

Besides the appearance and development of biofouling in the water distribution network, presence of BDOC produces other negative effects, i.e.:

- increasing use of disinfectants,
- intensification of electro-chemical corrosion of metals,
- colmatage and an increase in flow resistance,
- an increase in water pollution, reduced water quality,
- an increase in the amount of disinfection by-products,
- an increase in network exploitation costs [5, 9].

This paper presents research aimed at the assessment of BDOC during water disinfection process.

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 water supplied by the water company in the area comes exclusively from three aquifers, depending on the intake: Quaternary and Jurassic, including Upper Jurassic, Middle Jurassic and Triassic levels. The selected water supply pipeline covers an area of approximately 1000 km² 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 2308 km. It includes 9 storage tanks 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 Ø 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 14328.2 thousand m³/year, whereas the average water consumption is 121.3 L/person/day.

Water samples were taken from two water treatment stations. The first one is the oldest underground water intake, which began to operate in 1925-1928. At present water is drawn from a spring, which has been exploited since 1928 and
from 5 underground wells. The intake is from Upper Jurassic aquifer limestone rocks. Regular exanimated of water from first intake showed, that nitrate concentration increased by about 100 % and reached 80 mg NO$_3$/dm$^3$ whereas the permissible concentration is 50 mg NO$_3$/dm$^3$ in the period of 1995 to 2005. Apart from higher nitrates concentration the quality of uptaken water meets applicable standards in full. As a result this water treatment in A plant mainly involves biological denitrification (removal of nitrates) and ozonation. The second one is a multiple opening underground intake, which began to operate in 1974. It consists of 5 underground wells. The intake is from Upper Jurassic aquifer limestone rocks. Underground water drawn in this area has constantly had excellent natural physico-chemical and bacteriological properties during all the whole exploitation period. The drawn water is not treated due to its high quality. In order to maintain the stability of the bacteriological state during the distribution process, water is disinfected using chlorine.

The research also included the analysis of water samples taken from faucets at the consumers - the last point of distribution process. Water samples were collected for examination in the morning, around 8 (after the night stagnation, at a time of high water consumption). Samples were collected once a week for a month

### 2.2. Analytical procedure

The samples were collected in accordance with the standards set by the Polish Committee for Standardization [7]. Water from one intake station was treated with ozone, while water from the second intake was treated using sodium hypochlorite. Total organic carbon (TOC) was examined by TOC analyzer Multi N/C 2100. In order to obtain DOC fraction, water samples were filtered through a Ø 25 mm membrane filter with a 0.45µm sieve mesh diameter. Non-dissolved organic carbon (NDOC) and non-biodegradable dissolved organic carbon NBDOC were obtained by calculation methods. BDOC was determined using the Joret method, which involves observation of dissolved organic carbon (DOC) decrease in the examined water with a bacterial flora characteristic for the water. Biodegradable organic carbon (BOC) determined with this method indicates the amount of organic compounds which could potentially serve as a source of energy and support the growth of bacteria in the network. BOC measurement was performed in five days, therefore, this parameter characterizes a potential threat to water biostability well.
3. RESULTS AND DISCUSSION

All analyses were made three times. A standard deviation of the obtained results of TOC and DOC ranged from 0.01 to 0.06.

First raw water is taken from the source and one well. Then it undergoes ozonation in the treatment plant and next it is pumped to the water supply network in the pumping station.

Table 1 shows the amounts of different fractions of carbon. The range of TOC DOC and BDOC was 1.86-2.78 mg/L, 1.66-2.30 mg/L and 0.01-0.76 mg/L respectively. Non-dissolved organic carbon (NDOC) and non-biodegradable dissolved organic carbon (NBDOC) were obtained by calculation methods and were 0.10-0.57 mg/L and 0.90-2.20 mg/L respectively.

Table 1. The profile of raw water quality, the water from the water treatment plant and water distribution system-ozonated water

<table>
<thead>
<tr>
<th>Unit</th>
<th>Source</th>
<th>Well</th>
<th>Raw water</th>
<th>Pumping station</th>
<th>Consumer</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC</td>
<td>mg/L</td>
<td>2.25</td>
<td>2.78</td>
<td>2.52</td>
<td>2.40</td>
</tr>
<tr>
<td>DOC</td>
<td>mg/L</td>
<td>1.94</td>
<td>2.21</td>
<td>2.08</td>
<td>2.30</td>
</tr>
<tr>
<td>NDOC</td>
<td>mg/L</td>
<td>0.31</td>
<td>0.57</td>
<td>0.44</td>
<td>0.10</td>
</tr>
<tr>
<td>NBDOC</td>
<td>mg/L</td>
<td>1.86</td>
<td>2.20</td>
<td>2.03</td>
<td>2.13</td>
</tr>
<tr>
<td>BDOC</td>
<td>mg/L</td>
<td>0.08</td>
<td>0.01</td>
<td>0.05</td>
<td>0.17</td>
</tr>
</tbody>
</table>

When considering the percentage share of each organic carbon fraction detected in examined waters from the first intake (fig.1), it can be stated that the fraction having the largest share in TOC was DOC from 79.5% in the case of the well to 95.8% in the case of water from the pumping station; (TOC=DOC+NDOC), while in DOC the greatest fraction was NBDOC from 54.2% in the case of water from the consumer to 99.5% in the case of water from the well; (DOC=BDOC+NBDOC).

In raw water, it was non-biodegradable dissolved organic carbon which had the largest share of 2.03 mg/L. On the other hand, BDOC had the smallest share of 0.05 mg/L.

In examined water from the pumping station, NBDOC had the largest share (2.13 mg/L), whereas NDOC the smallest share of 0.10 mg/L.

An increase in the share of DOC in TOC after the disinfection process can be caused by the transformation of insoluble organic compounds to soluble forms, which has been confirmed in literature [10, 11].

In water taken from the taps at the consumers’, non-biodegradable dissolved organic carbon had the largest share of 0.90 mg/L, whereas NDOC had the smallest share of 0.20 mg/L.
The analysis of changes in BDOC contents in water taken from the first intake (fig. 2) showed that after ozone disinfection, the amount of BDOC increased from 0.05 mg/L to 0.17 mg/L (increase by 378%). This is due to the oxidation of sparingly soluble carbon compounds resulting in simpler forms that can be easily assimilated by microorganisms. The increase of the BDOC amount during the treatment processes has been confirmed in literature [4-6, 9, 14].

A significant change in the BDOC content was discovered during the distribution process – an increase of 447% (from 0.17 to 0.76 mg/L). This could be due to the poor condition the water supply network which may lead to the pollution of water by all kinds of chemicals.
The greater part of the water supply network runs through farmland and therefore soil solution with a high content of organic substances may leak into the pipeline.

Next raw water is taken from one well (no.10). Then it undergoes chlorination in the treatment plant and next it is pumped to the water supply network in the pumping station.

Table 2 shows the amount of different fractions of carbon. The range of total organic carbon, DOC and BDOC was 2.17-3.89 mg/L, 1.94-3.56 mg/L and 0.06-1.05 mg/L respectively. NDOC and NBDOC obtained by calculation methods were 0.09-0.84 mg/L and 0.89-2.54 mg/L respectively.

Table 2. The profile of raw water quality, the water from the water treatment plant and water distribution system - chlorinated water

<table>
<thead>
<tr>
<th>Unit</th>
<th>Well</th>
<th>Pumping station</th>
<th>Consumer</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC</td>
<td>mg/L</td>
<td>2.78</td>
<td>2.17</td>
</tr>
<tr>
<td>DOC</td>
<td>mg/L</td>
<td>1.94</td>
<td>2.08</td>
</tr>
<tr>
<td>NDOC</td>
<td>mg/L</td>
<td>0.84</td>
<td>0.09</td>
</tr>
<tr>
<td>NBDOC</td>
<td>mg/L</td>
<td>0.89</td>
<td>2.02</td>
</tr>
<tr>
<td>BDOC</td>
<td>mg/L</td>
<td>1.05</td>
<td>0.06</td>
</tr>
</tbody>
</table>

When considering the percentage share of each organic carbon fraction detected in examined waters from the second intake (fig.3), it can be stated that the fraction having the largest share in TOC was DOC(from 69,8 % in the case of water from the well to 95,8% in the case of water from the pumping station), while in DOC it was NBDOC ( 71,3% for consumer water and 97,1% for water from the pumping station), that had the largest share (except for raw water where BDOC fraction was the greatest and was 1.05mg/L).

In raw water, it was non-biodegradable dissolved organic carbon that had the largest share of 0.89 mg/L, whereas NDOC had the smallest share of 0.84 mg/L.

In the examined water from the pumping station, NBDOC had the largest share (2.02 mg/L), whereas BDOC the smallest share (0.06 mg/L).

An increase in the share of DOC in TOC after the disinfection process can be caused by the transformation of insoluble organic compounds to soluble forms, which has been confirmed in literature [9, 10].

In the water taken from the taps at the consumers’, non-biodegradable dissolved organic carbon had the largest share of 2.54 mg/L, whereas NDOC had the smallest share of 0.33 mg/L.

The analysis of changes in BDOC contents of water taken from the second intake (fig. 4) showed that after chloride disinfection, the amount of BDOC decreased from 1.05 mg/L to 0.06 mg/L (reduction by 94,3%). Similar studies were conducted by Kowal [5].
The author noticed an increase in the AOC (assimilated organic carbon) content in water during the process of oxidation using chlorine. The author indicated that the amount of AOC in water increased during the chlorine oxidation process, which is not confirmed by the results obtained for chlorinated water from the second intake. However, Raczyk-Stanisławik et al. (2008) claimed that in some waters biodegradability was lower than in raw water, probably due to the formation of chlorinated compounds with low biodegradability [8].

A significant change in the BDOC content was discovered during the distribution process – increase of 1700% (from 0.06 mg/L to 1.02 mg/L). This could be due to the poor condition of the water supply network which may lead to pollution of water by all kinds of chemicals. The greater part of the water supply network runs through farmland and therefore soil solution with a high content of organic substances may leak into the pipeline.
4. SUMMARY AND CONCLUSIONS

The comparison of the research results of water samples collected at the first and the second intake revealed that despite a similar TOC content in both raw waters, the share of individual fractions of organic carbon is different. The changes in the content of different forms of organic carbon in examined water largely depend on a method of the water treatment process and on the characteristics of raw water. The conducted studies show how much BDOC concentration differs depending on the applied method of disinfection. The use of ozone increased the content of BDOC and the use of chlorine decreased it. During both the ozonated water and chlorinated water distribution process, the content of BDOC in the water increased. The research led to the following conclusions:

- Natural organic matter, regardless of its quantity and origin, has a potential for formation of BDOC.
- Ozone water disinfection leads to the formation of organic products, which are almost completely absorbed by bacteria to a greater extent than in case of chlorine disinfection.
- the BDOC content in water adversely affects the microbiological safety of water.
- Forecasting and monitoring the BDOC content in tap water after water disinfection is important and helps to minimize the adverse impact of the BDOC presence in tap water on its quality and the condition of water supply network.

Obtaining biostability of water in water treatment processes is a condition for maintaining stability of the water composition in the water supply network and at the consumer’s. The water quality legislation does not determine the permissible concentration of individual fractions of carbon. The changes in BDOC in the water supply network should be routinely analyzed, since they are indicative of the likelihood of bacterial growth in the network. A detailed analysis of water supply network is also recommended, possibly supplemented with a model to facilitate its exploitation.

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REFERENCES


ZMIANY ZAWARTOŚCI BIODEGRADOWALNEJ MATERII ORGANICZNEJ W WODZIE WODOCIĄGOWEJ DLA MIASTA CZĘSTOCHOWY.

Streszczenie

Zawartość materii organicznej w wodzie może stanowić źródło węgla i energii dla wzrostu i rozwoju bakterii, co powoduje powstanie i rozwój biofilmu bakteryjnego w sieci wodociągowej. Dezynfektanty stosowane w celu zniszczenia drobnoustrojów lub zahamowania ich rozwoju działają zarówno na nie jak i na substancje chemiczne występujące w wodzie, zwiększając ich biodegradowalność. Powoduje to rozwój biofilmu bakteryjnego tworzącego się w sieci wodociągowej i wpływa niekorzystnie na jakość wody oraz stan sieci wodociągowej. Przedstawiono badania, których celem była ocena zmian zawartości biodegradowalnej materii organicznej podczas procesu dezynfekcji wody. Przedmiotem badań były próbki wody pobrane z ujęć, stacji pomp w stacji uzdatniania zlokalizowanych na terenie województwa śląskiego i od konsumenta. Źródłem zaopatrzenia w wodę na terenie objętym działalnością przedsiębiorstwa są wykluczenie wododolne eksploatowane w zależności od ujęcia z trzech pięter wodonośnych: czwartorzędu, jurajskiego, z poziomami wodonośnymi: górną, środkowojurajską oraz triasową. Wybrany wodociąg okręgu w województwie śląskim obejmuje swym zasięgiem powierzchnię około 1 000 km2, zaopatrując w wodę około 328,5 tys. mieszkańców. Jedną z wód dezynfekowano podchlorynem sodu, drugą ozonem. BRWO oznaczono wykorzystując metodę Joreta, która opiera się na obserwacji ubytku rozpuszczonego węgla organicznego RWO w badanej wodzie. Wykazano zmiany zawartości BRWO na poszczególnych etapach procesu uzdatniania i dystrybucji badanej wody wodociągowej i przeanalizowano biostabilność wody.

Słowa kluczowe: biodegradowalny rozpuszczony węgiel organiczny, wody podziemne, dezynfekcja, jakość wody

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