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Klaudia RAKOCZ, Agata ROSIŃSKA

Czestochowa University of Technology, Faculty of Infrastructure and Environment
Department of Chemistry, Water and Wastewater Technology
ul. Dąbrowskiego 69, 42-200 Częstochowa
e-mail: klaudiarakocz@o2.pl, rosinska@is.pcz.czest.pl

State of the Underground Water Illustrated with the Example of Water for Częstochowa City

Stan wód podziemnych na przykładzie wód dla miasta Częstochowa

The following thesis's objective is to analyze the quality of underground water for consumption, illustrated with an example of water for Czestochowa city. Although underground water is much better than surface water in terms of quality, it's 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 deliver 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. Sanitary safety is a major priority in water treatment process, whose main aim is assuring water biostability. Biological stability of water is confirmed by the content of BDOC (biodegradable dissolved organic carbon) and AOC (assimilable organic carbon). The permissible content of AOC and BDOC in non-chlorinated water is 3÷10 and 160 µg/L, respectively. The research results show that BDOC and AOC content in raw water was 20÷95 µg/L and 5÷19 µg/L, respectively. Therefore all examined waters met requirements for biostability in terms of BDOC content. In terms of AOC content, however, only 3 out of 6 waters met these requirements. Moreover the research results show that 47% of examined quality parameters classified underground water for Czestochowa city as first class water, 29% as second class, 18% as third class and 6% as fifth class. When treating underground water as drinking water, its quality parameters met the standards of water intended for human consumption, with the exception of nitrates concentration in the water from intake A's well, which was 62.1 mg/L and exceeded the acceptable concentration by 24%.

Keywords: **underground water quality, BDOC, AOC, treatment of underground water**

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 physico--chemical composition. However, surface water usually has a high content of substances with different properties, which change over time, and a different susceptibility to removal [1]. The content of underground water depends on the type and structure of rock, with which the water comes into contact, the degree of its erosion and granulation, the speed of underground water flow and the extent of contact with surface water and rain water [2].

Therefore, the treatment process of underground water requires simpler technological processes than surface water. During the exploitation of underground water intakes, unfavorable natural conditions such as rainfall and thaw may occur causing surface water, contaminated with various substances e.g. fertilizers, to come into contact with underground water. There are also emergencies such as traffic accidents and untreated sewage disposal, which lead to water contamination [3].

It is important to monitor underground water quality constantly, due to the fact that 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^3, while the underground water intake increased from 33% in 1980 to 70.4% in the year 2012, which is 1429.5 hm^3 [4].

Due to the growing importance of underground water use in the operation of the water distribution system, it is important to monitor underground water quality changes in the process of treatment in Poland. In terms of chemical and microbiological parameters, water quality is regulated by Polish law [5, 6].

One of the main threats to water quality is the growth and development of microorganisms in water supply network. Research conducted by Bonalam et al. and Chandy & Angels has shown that it is organic carbon that has the greatest impact on the development of biofouling forming in water supply network [7, 8]. Organic carbon, which occurs in water, can be divided into biodegradable fraction, i.e. BDOC, and refractive fraction, which does not affect the growth and development of biofouling in the network.

Besides the occurrence and development of biofouling in water distribution network, the 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,
- the increase in water pollution, reduced water quality,
- the increase in the amount of disinfection by-products,
- the increase in network exploitation costs.

The assimiliable fraction of organic carbon (AOC) constitutes a part of the BDOC fraction.

Whereas the content of total organic carbon (TOC) in water is standardized (the permissible value is 5 mg/L), its individual fractions responsible for the growth and development of biofouling in network (BDOC, AOC) are not [5]. However, their maximum values have been determined, which might lead to secondary water contamination in network, if they are exceeded. The permissible content of AOC and BDOC in non-chlorinated water is 3÷10 and 160 μg/L, respectively [9, 10].

The general characteristics of intake A

It 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 examination of water from intake A in the period of 1995 to 2005 showed that nitrate concentration increased by about 100% and reached 80 mg NO_3/dm^3 while the permissible concentration is 50 mg NO_3/dm^3. Apart from higher nitrate concentration, the quality of uptaken water fully complies with applicable standards. As a result, the water treatment in A plant mainly involves biological denitrification (removal of nitrates) and ozonation.

The general characteristics of intake B

It is the biggest, multiple opening underground intake, which began to operate in 1955. It consists of 18 underground wells. The intake is from Upper Jurassic aquifer limestone rocks. Raw water from intake B, which is taken from several wells, is stored in two tanks: left and right. The threat to the quality of water drawn from intake B is a low degree of isolation of the aquifer in the form of poorly permeable rock cover (approx. 50%). Therefore, the underground water reservoir is continuously contaminated by run-off from the surface.

In terms of its physicochemical and microbiological state, water delivered to the water supply network from intake B is very good because all the physico-chemical and bacteriological indicators fully meet the requirements set by Polish standards. As a result of its high quality, water from intake B is not currently treated. In order to maintain bacteriological stability during the distribution process, the water is disinfected using only ozone.

The general characteristics of intake C

It 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 physicochemical and bacteriological properties throughout the whole exploitation period. The drawn water is not treated because of its high quality. In order to maintain the stability of the bacteriological state during the distribution process, water is disinfected using sodium hypochlorite.

The general characteristics of intake D

It is an auxiliary intake of the examined city, which delivers water from Triassic aquifer (limestone, dolomite). The water, which is drawn from that intake through one well, has an abnormal concentration of iron and manganese (geogenic contamination), thus it has to be treated.

The water treatment process consists of the following stages:

- aeration of water (oxidation of iron compounds present in raw water),
- de-ironization,
- disinfection by sodium subchloride solution.

1. Materials and methods

1.1. Materials

To conduct the research, water samples were taken from water intake points, which include springs and wells for the particular water treatment plants located in the city of Czestochowa and its vicinity, Silesia voivodeship, Poland. The samples were collected in accordance with standards set by the Polish Committee for Standardization (Polish Standards and Polish Standardization Documents). Examined water, which was from the intake stations marked A and B was treated with ozone, while water from the intake stations C and D was treated using sodium subchloride.

1.2. Analytical procedure

Water samples were collected for examination in the morning, around 8 a.m. (after nighttime stagnation, at a time of high water consumption), in accordance with the applicable standards of the Polish Committee for Standardization. The samples underwent a physicochemical analysis. The typical physicochemical indicators were determined.

In order to assess the water quality, selected physicochemical water quality indicators were used, which were identified in accordance with the applicable standards of the Polish Committee for Standardization.

BDOC was examined using own method based on Joret method (the change was the collection of microorganisms and inoculation to the water samples), while AOC was examined according to Standards Methods. In order to obtain DOC fraction, water samples were filtered through a Ø 25 mm membrane filter with a 0.45 μm sieve mesh diameter. General number of microorganism was determined by heterotrophic plate counts method (HPC). Coliform count was determined by fermentation test.

2. Results and discussion

The analysis of the selected quality parameters of water (Table 1) showed that the chemical state of underground water is good, and it was shown that the water does not exceed threshold concentration for good state of underground water, specified in the Minister of Environment Regulation 2015 [6]. The only exception is magnesium content in tap water D, which totaled 216.0 mg/dm^3. As a result, the water is classified as fifth quality class, which means poor chemical state of examined water.

The analysis of the selected physical quality parameters of water (Table 1) showed that:

– the odor in all water samples was acceptable. It had a very weak plant smell. The exception was the water from the well of intake D, which had the specific smell of hydrogen sulfide in the 3rd degree. Biłozor et al. claim that the presence of hydrogen sulfide in water may be caused by the biochemical decomposition of organic matter and reduction of sulfides [11];
– in water from intakes A, B and C, turbidity was 0.3÷0.31 NTU, and general iron content totaled up to 40 µg/dm^3, while in the case of water D intake turbidity was 0.82 NTU, and general iron content totaled 230 µg/dm^3. According to literature sources, turbidity is correlated with iron content in water, which is proven by the above-mentioned results. The higher the content of this element, the higher the turbidity [12, 13];
– the color of D water was 5 Pt/dm^3, whereas in other samples this indicator did not reach the limit of quantification.

pH value - one of the analyzed chemical indicators of quality of examined raw water - totaled 7.7 and 7.8. The range of pH value characteristic for underground water was 6.5÷8.5. The value of pH indicates physicochemical conditions of migration of substances in underground water, including toxins. Therefore, the assessment of pH value may be made not only in terms of its value but also in terms of the possibility of toxic contamination of underground water [14].

Another analyzed indicator of the examined water was nitrogen in three forms: ammonium nitrogen, nitrate nitrogen and nitrite nitrogen. Nitrogen mostly occurs in underground water as nitrate [1, 6]. The content of ammonium ion and nitrites did not reach the limit of quantification. According to Kowal and Świderska-Bróż [2], the occurrence of only nitrates proves that water was contaminated a long time ago. The presence of nitrate in water is mostly caused by human impact, such as the use of mineral nitrogen fertilizers and liquid manure and the transfer of municipal liquid waste to underground water in rural areas with no sewerage system [15]. Ammonium ion is the main indicator of the level of degradation of the Jurassic reservoir of underground water [16, 17]. The presence of nitrogen in drainage basin may also be caused by rainfall [18]. Nitrate content in the examined waters exceeds the values of characteristic concentrations according to the Minister of Environment's Regulation. It amounted to 0÷5 mg/dm^3, except for the water from intake D, in which nitrate content was 0.46 mg/dm^3. Water from intake B contained 16.9 and 18.3 mg/dm^3 nitrate.

Table 1. **The profile of raw water quality**

Parameters	Unit	A		B		C	D
		Spring	Well	Left tank	Right tank		
Turbidity	NTU	0.30	0.30	0.30	0.31	0.30	0.82
Color	Pt/dm^3	< 5	< 5	< 5	< 5	< 5	5
Smell		z1R	z1R	z1R	z1R	z1R	z3S(H_2S)
pH	pH	7.7	7.8	7.7	7.8	7.7	7.8
Ammonium ion	mg/L	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	<0.05
Nitrites	mg/L	< 0,018	< 0.018	< 0.018	< 0.018	< 0.018	<0.018
Nitrates	mg/L	49.3	62.1	18.3	16.9	48.3	0.46
Permanganate index	mg/L	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50
Chlorides	mg/L	29.5	27.3	23.6	11.9	25.0	11.8
General iron	µg/L	< 40	< 40	< 40	< 40	40	230
Manganese	µg/L					< 10	55
Sulfates	mg/L					49.0	47.0
General hardness	mval/L	4.20	4.02	3.74	3.40	4.54	3.84
Alkalinity	mval/L	2.28	1.74	2.60	2.60	2.64	3.18
Non-carbonate hardness	mval/L	1.92	2.26	1.14	0.80	1.90	0.66
Calcium	mg/L					87.0	50.5
Magnesium	mg/L					2.43	216.0
Phosphates	mg/L						0.178
Free carbon dioxide	mg/L	6.6	4.4	8.8	6.6	7.6	8.8
Dissolved oxygen	mg/L	7.61	8.62	8.21	8.94	6.23	2.55
Fluoride	mg/L					< 0.20	0.66
Phenols	mg/L					< 0.001	< 0.001
Conductivity	µS/cm	483	462	483	462	497	432
TOC	mg/L	1.25	0.78	1.25	0.78	1.78	1.16

The content of chloride ions in the examined waters was from 11.8 to 29.5 mg/dm^3. The content of chloride ions is directly proportional to the degree of mineralization of underground water [15].

Manganese content from intake D amounted to 55 mg/dm^3. Manganese usually occurs in natural water together with iron, but in much smaller quantities, and its concentration increases along with water mineralization [1, 6].

Sulfate content from intakes C and D amounted to 49 and 47 mg/dm^3 respectively.

A and C intakes yielded medium-hard waters, while B and D intakes were soft waters according to the water hardness scale [19].

Alkalinity amounted to 1.74÷3.18 mval/dm^3. Non-carbonate hardness amounted to 0.66÷2.26 mval/dm^3.

Calcium content from intakes C and D amounted to 87 and 50.5 mg/dm^3 respectively. Calcium ions are dominant cations in underground water. They are involved in ion exchange, determine the hardness of water and thus it is useful for industrial purposes [1, 6].

Magnesium content from intake C (2.43 mg/dm^3) classified the water as first class water, while in the case of D (216.0 mg/dm^3), it classified the water as fifth class. According to Kowal and Świderska-Bróż [2], the ratio of calcium ions to magnesium ions is usually constant and varies depending on the degree of mineralization. However, such correlation could not be observed in the examined waters. Phosphate content from intake D was 0.178 mg/dm^3. Phosphates are the most common form in which phosphorus compounds occur in underground water. Phosphate content is a biophilous parameter - it is the primary nutrient for living organisms [14].

Free carbon dioxide content ranged from 4.4 to 8.8 mg/dm^3 in the analyzed samples. Kowal and Świderska-Bróż [2] reported that as water carbonate hardness increases, so too does the amount of carbon dioxide. This dependency was noticed in the examined waters. Carbon dioxide plays a key role in the underground water chemistry formation. On the one hand, it enhances dissolution of many minerals by water, and on the other it is the source of HCO^{3-} ions as it dissolves in water itself [1, 6].

Dissolved oxygen content, which ranged from 6.23 mg/dm^3 for intake C water to 8.94 mg/dm^3 for the right reservoir of intake B water, exceeded the characteristic concentration set out in the Ministry of Environmental Regulation (0÷5 mg/dm^3). Only in the case of intake D water, the content of dissolved oxygen was lower and amounted to 2.55 mg/dm^3. According to Kowal et al., dissolved oxygen is one of the main ingredients which shape the content of underground water because its amount determines the conditions for oxidation and reduction and influences a lot of the chemical and physical processes [1, 6].

The detected amount of fluorides was 0.66 mg/dm^3 from intake D.

Total organic carbon content (TOC) is a general parameter, which provides information on the presence of organic substances in underground water. In the examined samples the content of TOC was 0.78÷1.78 mg/dm^3. These values are low and indicate a very good state of these waters.

The next parameter is conductivity. It indicates the amount of free ions in the examined solution and was 432÷497 μS/cm. Phenol content and permanganate index did not exceed the level of quantification.

When considering and comparing the requirements for quality parameters set out in the Ministry of Environmental Regulation of 2015 with the detected parameter values of examined waters, it can be stated (Fig. 1) that 8 underground water quality parameters classified the waters as first class (these parameters make up 47% of all the examined parameters), 5 parameters classified the water as second class (these make up 29.4% of all the examined parameters), 3 parameters classified the waters as third class (17.6% of all the examined parameters) and 1 parameter classified the waters as fifth class (6% of all the examined parameters).

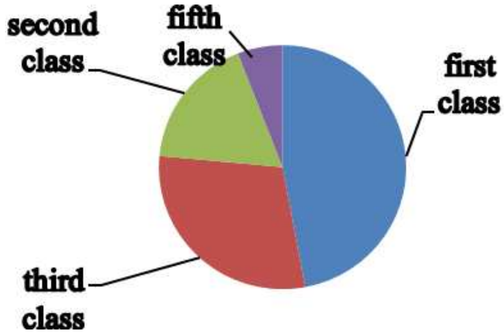

Fig. 1. The share of chemical quality parameters of waters of different quality class

When the parameter values of examined waters were compared to requirements for water for human consumption, it was determined that the values of the physico--chemical parameters of the quality of water were in accordance with the requirements set for water for human consumption, except for excessive nitrate content in the water from intake station A, which was 62.1 mg/dm^3 and exceeded acceptable concentration by 24% [5]. This leads to the conclusion that B, C and D raw underground waters can be consumed by humans.

In terms of microbiological properties, it was determined that bacteriological quality of all examined waters met applicable national standards. The value of colony forming units is shown in Table 2. According to Biłozor et al. [11], underground water is virtually free of pathogenic microbes and even if such contamination takes place, it is mostly caused by a technical defect of the well.

Table 2. **The microbiological state of examined underground water**

Parameters	Unit	A		B		C	D
		Spring	Well	Left tank	Right tank		
General number of microorganism in temp. 22 ± 2°C after 68 ± 4 h	CFU/mL	54	10	14	13	9	6
General number of microorganism in temp. 36 ± 2°C after 44 ± 4 h	CFU/mL	4	3	3	3	3	5
Coliform count (NPL)	CFU/100 mL	0	0	0	0	0	0

The largest number of microorganisms in 22°C was detected in the water from A intake's spring (54 CFU/mL). However, the number of those microorganisms in A intake's well was 10. In the case of B intake water, the number of microorganisms in both reservoirs was nearly identical (13 and 14 CFU/mL). The lowest number of microorganisms was detected in C intake water (9 CFU/mL) and D intake water (6 CFU/mL). The number of microorganisms in 36°C was similar in all examined samples and ranged from 3 CFU/mL do 5 CFU/mL. No coliforms were detected in any samples. After examining coliforms, which is a key indicator of sanitary water abandoned examine *Enterococcus faecalis*, because it was considered that the lack of coliforms and a low content of the general number of microorganisms are sufficient to determine the microbiological state of tested waters.

However, the threat of development of a higher number of microorganisms and of the growth and development of biofouling in water supply network is illustrated by such parameters as BDOC and AOC. The values in the table below (Table 3) are presented in comparison to the water biostability requirement specified in the literature (it is 3÷10 μg/L for AOC in non-chlorinated water and 160 μg/L for BDOC). Taking the values into account, all examined waters met the abovementioned requirement in terms of BDOC content [9, 10]. However, in terms of AOC content, only half of the examined waters met the requirement. Thus the unstable waters were: water from intake A's spring, water from intake B's left tank and water from intake C. It is of major significance because even in high quality water (which undoubtedly is underground water), when permissible values of BDOC and AOC are exceeded, the threat of secondary contamination is highly probable, as according to Volk and LeChevallier, microorganisms can grow in water containing only trace amounts of nutrient substrates [10].

Table 3. **The content of biodegradable fractions of organic carbon in examined underground waters**

Parameters	Unit	A		B		C	D
		Spring	Well	Left tank	Right tank		
TOC	mg/L	1.25	0.78	1.25	0.78	1.78	1.16
DOC	mg/L	0.85	0.5	0.86	0.48	1.20	0.74
BDOC	μg/L	80	20	85	35	95	65
AOC	μg/L	17	5	19	7	12	10

The content of TOC in all examined raw waters ranged from 0.78 to 1.78 mg/L. The share of DOC in TOC was from 61.5 to 68.8%. AOC constituted from 12.63 to 25% of BDOC. BDOC and AOC constituted from 2.56 to 6.8% and from 0.64 to 1.52% of TOC respectively.

A similar analysis was conducted for underground water in Poznan and Pila, where the content of TOC amounted to 4.85 and 4.58 mg/L respectively. However, the content of BDOC was 0.3 and 0.25 mg/L respectively [20]. This proved that the waters were unstable biologically.

According to Lehtola M. et al., the content of TOC ranged from 0.7÷1.8 mg/L, while the content of AOC amounted to 23÷68 μm/L in the waters of Finland [21]. This also proved that the waters were unstable biologically in terms of AOC content, while BDOC content almost exceeded the permissible maximum value regarding stability.

Summary and conclusions

Water for human consumption in the city of Czestochowa is drawn from underground reservoirs, which formed in Upper and Middle Jurassic period and are in contact mainly with limestones. As a result, water delivered to consumers has physicochemical composition which is advantageous for health.

The conducted research showed that:

- examined water does not contain excessive amounts of minerals (low-sodium and low-chlorides water);
- examined water contains from 50.5 to 87 mg Ca/dm^3 of calcium;
- 94.1% of all identified water quality parameters fall into the 1st, 2nd and 3rd class of water, with the exception of content of magnesium in the water from intake D (216.0 mg/dm^3, which represents 5.9% of examined water parameters) which classified the water as fifth class in terms of the content of this element;
- all of the examined waters could be classified as drinkable except for the water from intake A's well because the nitrate concentration was 62.1 mg/dm^3 and was 24% higher than the permissible value;
- water is chemically stable;
- examined water doesn't contain coliform microorganism;
- natural organic matter, regardless of its quantity and origin, has a potential for formation of BDOC;
- all examined waters meet the requirement for biological stability in terms of BDOC content; however, only half of the waters meet the requirement in terms of AOC content.

Organoleptic tests show that produced water is clear, transparent, colorless and very tasty in its natural state. It owes its refreshing taste to the presence of calcium and magnesium in suitable proportions.

Despite the high quality of drawn underground water, the water which is delivered to water supply system is disinfected with ozone (intakes A and B) and chlorinated (other intakes). Disinfection of water is necessary because it prevents infections and secondary bacterial growth in the water distribution 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. The water quality legislation does not determine the permissible concentration of individual fractions of carbon. The changes in BDOC in 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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Streszczenie

Celem niniejszej pracy jest analiza jakości wód podziemnych ujmowanych na cele konsumpcyjne na przykładzie wody dla miasta Częstochowa. Chociaż pod względem jakości woda podziemna jest znacznie lepsza od wody powierzchniowej, konieczne jest monitorowanie jej jakości cały czas, ponieważ może ulegać ona obniżeniu podczas eksploatacji ujęć z wielu powodów. Jest to o tyle istotne, iż nastąpiły zmiany w spożyciu wody w ciągu ostatnich 30 lat w Polsce. Dotyczyły one wzrostu udziału wód podziemnych w ogólnej ilości eksploatowanych zasobów wodnych do 70,4% do 2012 roku. Woda pitna jest dostarczana głównie do konsumentów przez przedsiębiorstwa wodociągowe, których obowiązki obejmują czerpanie wody ze źródeł naturalnych i przygotowanie jej w taki sposób, aby była ona nieszkodliwa dla odbiorców. Wybór metody i technologii uzdatniania wody zależą głównie od jakości wody surowej. Priorytetem w procesie uzdatniania wody jest zapewnienie bezpieczeństwa sanitarnego wody. Innymi słowy, głównym celem jest zapewnienie biostabilności wody. O stabilności biologicznej wody świadczy przede wszystkim zawartość BRWO (biodegradowalny rozpuszczony węgiel organiczny) i PWO (przyswajalny węgiel organiczny). Dopuszczalna zawartość BRWO i PWO w wodzie niechlorowanej wynosi odpowiednio 160 i 3÷10 µg/l. Wyniki badań pokazują, że zawartość BRWO i PWO w wodzie surowej wynosiła 5÷19 i 20÷95 µg/l. Dlatego wszystkie badane wody spełniały wymagania dotyczące biostabilności pod względem zawartości BRWO. Jednakże pod względem zawartości PWO tylko 3 z 6 badanych wód spełniały te wymagania. Ponadto wyniki badań pokazują, że 47% analizowanych parametrów jakościowych wód podziemnych dla miasta Częstochowa sklasyfikowano w pierwszej klasy wód, 29% w drugiej klasie, 18% w trzeciej klasie, a 6% w piątej klasie. Rozważając wody podziemne jako wody pitne, ich parametry jakościowe spełniały standardy wody przeznaczonej do spożycia przez ludzi z wyjątkiem stężenia azotanów w wodzie ze studni A, które wynosiło 62,1 mg/l, i przekroczyło dopuszczalne stężenie o 24%.

Słowa kluczowe: **jakość wód podziemnych, BRWO, PWO, oczyszczanie wód podziemnych**