Nitrification Activity of Water Sources in Dnipropetrovsk Region (Ukraine)

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To cite this article: Hryhorenko Liubov Victorovna. Nitrification Activity of Water Sources in Dnipropetrovsk Region (Ukraine). Hydrology. Vol. 5, No. 5, 2017, pp. 67-72. doi: 10.11648/j.hyd.20170505.11

Received: January 28, 2017; Accepted: February 13, 2017; Published: October 23, 2017

Abstract: In the decentralized water supply sources all tacsons, except 6 tacson, had an unfavorable self-purification processes and incompleteness of nitrification activity. Therefore the average annual indicators in the water samples, carried out in 1 – 5 tacsons, increased in dynamics by the nitrogen ammonia: from (0.24±0.05) to (0.43±0.20) mg/dm$^3$, i.e. in 2.0 times, in comparison with content of nitrates: (5.95±0.06) to (14.72±5.57) mg/dm$^3$, which increased in 2.5 times (p < 0.001).

It was proved that water from decentralized sources in the 1 – 5 tacsons of Dnipropetrovsk region did not correspond to the GOST 7525:2014 caused by the high concentration of nitrites and nitrates between 2008 and 2014 year. Thus, according to the average annual indicators was identified high level of nitrites (42.5 MAC), nitrates (1.2 MAC) in the 1 tacson; (1.4 MAC) of nitrites and (2.0 MAC) of nitrates in the 4 tacson. Unfavorable nitrification activity in the decentralized drinking water sources in all tacsons of Dnipropetrovsk region, except 6 tacson, in 2008 – 2014 years was shown incompleteness of the self-purification water in the rural settlements, causing primary morbidity among peasants as well as the blood and blood – forming organs, methemoglobinemia among infants due to a consumption of water from wells. In the centralized water supply sources of all tacsons was identified poor self-purification, as well as nitrogen ammonia decreased in dynamics for 2008 – 2014 years, while nitrites and nitrates contents increased. Only in the 2 tacson was significant decreased in dynamics of ammonia nitrogen (1.2 MAC) against rising of the nitrates levels (2.3 MAC) (p < 0.001). However, overnormal oxidation (1.09 MAC) in 2014, with increasing in dynamics for 2008 to 2014 year described organic nature of pollution in the given tacson. All tacsons of Dnipropetrovsk region, except 2 tacson, did not correspond to some indicators: 1 tacson – nitrites (30.9 MAC) in 2012; 3 tacson – nitrogen ammonia (1.06 – 1.52) MAC in 2009, 2011, (1.42 MAC) in 2012, 2013, (1.36 MAC) in 2014; 4 tacson – oxidation (1.33 – 1.15) MAC in 2008, 2014; 5 tacson – nitrogen ammonia (1.02 MAC) in 2011, nitrites (1.6 MAC) in 2014, oxidation (1.21 MAC) in 2010. Recommended collective installations of drinking water purifiers, primarily in the medical – preventive and children's educational institutions in all rural tacsons of Dnipropetrovsk region.

Keywords: Nitrates Activity, Drinking Water, Self – Purification, Decentralized Sources, Rural Tacsons

1. Introduction

Officially, Dnipropetrovsk region has such water resources: superficial – 0.24 thousands m$^3$/ year per 1 person (average index in Ukraine 1.02 000 m$^3$/ year per 1 person); underground – 0.12 thousands m$^3$/ year per 1 person (in Ukraine standard indicator 0.44 thousands m$^3$/ year per 1 person). Generally, the centralized water-supply system covers about 20 cities, 270 rural settlements [1, 2].

In Dnipropetrovsk region are determined 296 water plumbings with power 2993.80 thousands m$^3$/ per 1 day. The volume of drinking water carried out to the municipal network in 2008 was 809.88 million m$^3$ from centralized system; 9.54 million m$^3$ from decentralized water supply system [3]. In order to support rural population with high quality drinking water was provided 16 superficial water intakes with power 486.10 millions m$^3$/ year (river Dniper and Karachunivskyi reservoir, channels "Dniper-Donbas", "Dniper-Kryvyi Rih", "Dniper-Inhulets", "Dniper – West Dnosoph" and numerous small water intakes); 107 underground water intakes with power 13.52 millions m$^3$/ year, and 98 mining wells with power 2.18 millions m$^3$/ year [4].

Dnipropetrovsk region was covered with centralized water systems on 69.7%, however in large cities the regional index was 50% higher than in Dnipropetrovsk region, in the cities this index was varied from 14.9 to 48.2%, in the rural settlements – from 0.8 to 100%. Index of support population
with good quality drinking water in the cities was determined 209 litres / per 1 day, in the rural settlements 38 litres / per 1 day [5]. In the Dnipropetrovsk region about 19% rural settlements were covered with centralized water supply system with numerous infringements during exploitation. Majority of rural settlements: 626 settlements used drinking water from mine wells, well – known as unprotected superficial aquiferous horizon. Peasants living in 267 rural settlements, i.e. 61 thousand people were supported with bottled water, which is transfer from special transport from large cities [6].

Basic problems of standard quality water supply: absent of high quality drinking water, contamination of superficial reservoirs, mineral salt increasing, poor quality of underground water sources, troubles with network system 25 – 40%, the post – Soviet Union technologies of water treatment. Officially, Ukraine indexes, calculated on the quantity of population in Dnipropetrovsk region the government carried out for drinking water purposes around 1777.08 million m³/year (4868.71 thousand m³/per 1 day), for sanitary – epidemiological purposes – 453.69 million m³/year (1242.99 thousand m³/year), for agricultural purposes – 38.96 million m³/year, for landscape gardening – 5.26 million m³/year, etc. [7]. Structure of water consumption and water disposal: for apartments, which were supported with centralized systems of water supply, sewage system and hot water – supply should be 280 litres /per 1 day; for rural apartments with the same systems and local source of water supply should be covered 200 litres /per 1 day [8].

The Ukrainian government carried out about 66.6% population with centralized disposal systems and about 52% peasants in the rural settlements. As a result, the large cities should be covered with sewage system, according to hygienic standards – from 50 to 98.4%, in the provinces – from 5 to 47.6%, in the rural settlements – from 0.8% in Yurievskyi district to 100% in Dneprodzerzhynsk city. Pavlogradsky and Tomakovskyi rural districts did not have water disposal system [9].

Reports of outbreaks in Canada and the United States (U.S.) indicate that approximately 50% of all waterborne diseases occur in small non-community drinking water systems [10].

Safe potable water is essential for good health. Worldwide, school-aged children especially in the developing countries are suffering from various water-borne diseases [11].

Housing livestock on the property, using a shore well, and having a well located in gravel or clay soil increases the risk of having antimicrobial resistant E. coli in E. coli contaminated wells [12]. To reduce the incidence of water borne disease and the transmission of antimicrobial resistant bacteria, owners of private wells need to take measures to prevent contamination of their drinking water, routinely test their wells for contamination, and use treatments that eliminate bacteria [13].

Water samples submitted for bacteriological testing in Ontario and Alberta Canada were tested for E. coli contamination, with a portion of the positive isolates tested for antimicrobial resistance [14]. Households were invited to complete questionnaires to determine putative risk factors for well contamination [15].

Drinking more water and/or replacing sugary beverages with water also may help reduce obesity and dental problems among children and adolescents. Starting in the 2011-12 school year, schools participating in the federally-funded National School Lunch Program were required to provide students with access to free drinking water during school meals, in the location where meals are served [16]. Thus, this research aimed to describe dynamics of nitrification activity in the centralized and decentralized water supply sources in the rural tacsons of Dnipropetrovsk region during 2008 – 2014 years.

2. Materials and Methods

In our research water quality indicators were determined, using sanitary – toxicological methods: nitrogen ammonia, nitrates and nitrites concentrations (general quantity of laboratory research carried out in the centralized sources – 38 260; in the decentralized water sources – 24 586). Quantity of research was calculated, based on the general quantity of water supply sources, which was varied in the different types of rural tacsons in Dnipropetrovsk region.

Nitrification activity in the both types of drinking water sources for 2008 – 2014 years was investigated, according to the requirements of National Standard ISO 7525:2014 [17] and State Sanitary Norms and Rules 2.2.4-171-10 [18].

Taking into account the territorial distribution all rural settlements in Dnipropetrovsk region have been classified into 6 types of tacsons, according to the "Geographical map of Dnipropetrovsk region". Statistical characteristics included: number of observation objects (n), arithmetic meaning (M), standard error (m), median (Me). Statistical criteria: Student t-test, Mann-Whitney test, $\chi^2$ — Pearson. In order to identify characteristic differences for quantitative data depending on the action of environmental factors we carried out analysis of variance in the procedure "ANOVA".

We carried out statistical processing in the package "STATISTICA" version 6.1. (serial number AGAR 909 R455721FA).

3. Results and Discussion

Indicators of nitrification activity in the drinking water of centralized water sources of 1 tacson (nitrogen ammonia, nitrates and nitrites) should not increase maximum admissible concentration (MAC), except in 2012 year. Overnormal concentration of nitrates (15.45±0.04) mg/dm³ – 30.9 MAC and oxidation (5.57±0.08) mg/dm³ – 1.11 MAC was revealed in 2012. Nitrites content in the drinking water was significantly increased 1.7 times in terms of dynamics: from (0.018±0.005) to (0.031±0.014) mg/dm³. In this case, an average annual indicator for nitrites was on the level: 2.22±0.02 mg/dm³, i.e. 4.44 MAC.

In the surface sources was shown tendency to decreasing level of nitrates and ammonia nitrogen during 6 – year period, indicating the adverse dynamics of self-cleaning of drinking water in the 1 rural tacson. On the one hand, the ammonia nitrogen decreased: from (0.31±0.08) mg/dm³ in 2008 to (0.22±0.06) mg/dm³ in 2013, thereafter that was growing to the initial level: (0.31±0.05) mg/dm³ in 2014 (p = 0.243). On
the other hand, at the same period of observation nitrates content was decreased significantly 2.6 times: from (2.80±0.80) to (1.07±0.39) mg/dm$^3$ (p<0.001). Oxidizability in the drinking water of 1 tacson was increased 4.8 times in dynamics from (0.84±0.21) to (4.04±0.83) mgO$_2$/dm$^3$ (p = 0.227; p<0.001) between 2008 and 2014 years. This trend should prove process of constant organic contamination carried out in the centralized drinking water sources of 1 tacson.

Indicators of nitrification activity (ammonia nitrogen, nitrites and nitrates) shows self-purification processes typical for the centralized sources in 2 tacson, because dynamics between 2008 and 2014 year have been shown decrease of ammonia nitrogen and increase of nitrates concentrations, which clearly indicates the nitrification activity occurring in the drinking water sources.

So, nitrogen of ammonia in the drinking water was significantly decreased 1.2 times from (0.19±0.01) to (0.16±0.03) mg/dm$^3$ (p = 0.243; p<0.001). While the nitrates in dynamics was significantly increased 2.3 times: from (1.07±0.47) to (2.50±0.25) mg/dm$^3$ (p<0.001). However, increasing of oxidation in terms of dynamics for the same period should indicate the high content of organic substances in the drinking water. It demonstrated a slight deviation value from: 1.09 MAC in 2014, to the highest value which was observed in 2014: 5.47±0.48 mg O$_2$/dm$^3$.

In the surface drinking water sources of 3 tacson was shown an overnormal average annual concentration of ammonia nitrogen: 1.06 MAC (in 2009), 1.52 MAC (in 2011). The same tendency was characterized for oxidation: 1.42 MAC (in 2012 – 2013), 1.36 MAC (in 2014), which probably indicates an extremely high intake of organic substances into the centralized water supply sources. At the same moment, an unfavorable dynamics of water self-purification was carried out. Thus, a significant decrease of nitrogen ammonia on a background of decreasing the nitrates content was determined. Therefore, the content of ammonia nitrogen was reduced from (0.34±0.03) to (0.17±0.03) mg/dm$^3$ (p = 0.258) on a background of nitrates decreased 1.3 times: from (3.18±0.27) to (2.44±0.41) mg/dm$^3$ (p = 0.229; p<0.001). Simultaneously, it was observed an unfavorable trend to increasing level of nitrites 47 times: from (0.017±0.002) to (0.80±0.08) mg/dm$^3$ (p<0.001), nitrates 1.13 times: from (6.38±0.52) to (7.23±0.63) mg/dm$^3$ (p<0.001). The trend to decrease oxidation has been shown low level of organic substances in the drinking water sources. From time to time was observed significantly increasing some indicators such as ammonia nitrogen: 0.51±0.09 mg/dm$^3$ (p<0.001), i.e. 1.02 MAC (in 2011), nitrates: 0.80±0.08 mg/dm$^3$ (p<0.001), i.e. 1.6 MAC (in 2014) and oxidability: 6.06±0.46 mgO$_2$/dm$^3$ (p<0.001), i.e. 1.21 MAC (in 2010).

Unfavourable nitrification activity carried out in the 6 tacson centralized water supply sources. Generally, territory of the 6 tacson includes 8 rural districts (Apostolovskiy, Magdalovskiy, Petropavlovskiy and Pokrovskiy, Solonianskiy, Tomakovskiy, Tsarychanskiy and Yurievskiy) of Dnipropetrovsk region. Thus, in the surface water sources were determined significant decreased of the ammonia nitrogen, nitrites, nitrates and oxidation. Decreasing of ammonia nitrogen 2.9 times has been shown between 2008 and 2014 years: 0.12±0.01 mg/dm$^3$ (p<0.001), nitrites decreased 1.6 times: 2.71±0.53 mg/dm$^3$ (p<0.001), nitrates decreased 5.6 times: 0.005±0.002 mg/dm$^3$ (p<0.001). Results of our research have been shown trend to constantly increasing of oxidation: 5.88±0.24 mgO$_2$/dm$^3$ (p<0.001), i.e. 1.18 MAC in 2010, 5.55±0.47 mgO$_2$/dm$^3$ (p<0.001), i.e. 1.11 MAC in 2013.

The given trend demonstrates an unfavorable self-cleaning activity of water in the majority of rural tacsons, because the ammonia nitrogen, nitrites, nitrates, oxidation decreased in terms of dynamics (Figure 1).

The same trend of poor self-purification process in the decentralized water sources was shown in the 1 tacson. Data of our research demonstrated significant increasing of the ammonia nitrogen and nitrates, and decreasing of nitrates, according to the ISO 7525:2014 requirements for underground water sources. In this tacson level of ammonia nitrogen increased 1.4 times: from (0.23±0.02) to (0.32±0.07) mg/dm$^3$ (p=0.243; p<0.001). The given trend was typical for nitrites in the underground water sources some years: in 2008 (1.65 MAC); in 2009 (1.25 MAC); in 2012 (3.0 MAC); in 2013 (1.5 MAC); in 2014 (3.05 MAC). Level of an average annual indicator of nitrites increased (42.5 MAC). Therefore, nitrites increased 1.75 times in the underground sources: from (8.08+0.89) to (4.60±0.02) mg/dm$^3$ (p<0.05). However, in the 1 tacson from time to time was observed nitrites increased: in 2008 (1.6 MAC); in 2010 (2.7 MAC); in 2011 (1.7 MAC); an average annual indicator level (1.2 MAC).

So, in the 2 tacson decentralized water supply sources have been shown unfavorable self-purification processes. The results of the analysis suggest trend to decreasing ammonia nitrogen, nitrites, nitrates between 2008 and 2014 years. However, it has been shown increased of ammonia nitrogen: (1.6 – 2.0) MAC between 2008 and 2010; nitrites (2.0 – 3.0) MAC between 2008 and 2013 years; nitrates (3.5 – 4.0) MAC between 2008 and 2011 years. Consequently, ammonia nitrogen was significantly decreased 2.0 times.
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from (0.24±0.16) to (0.14±0.07) mg/dm$^3$ (p<0.001). Similar trend was revealed in this tacson for nitrates, which increased 4.1 times in terms of dynamics: from (9.47±0.54) to (2.29±0.006) mg/dm$^3$ (p<0.001). Thus, the highest content of nitrates was shown in 2010: 13.31±3.95 mg/dm$^3$, the lowest content (< 5.0 mg/dm$^3$) in 2012.

Figure 1. Dynamics of nitrification activity and oxidation in the centralized water supply sources in the rural tacsons of Dnipropetrovsk region (by the average annual indicators).

Results of monitoring drinking water quality in the 3 tacson demonstrate an unfavorable nitrification activity in the decentralized sources by the ammonia nitrogen and nitrites levels. Thus, it was revealed level of ammonia nitrogen in 2008: 0.23±0.02 mg/dm$^3$, which was significantly increasing in 2010: 0.37±0.11 mg/dm$^3$, thereafter decreased 1.3 times in 2014: 0.17±0.01 mg/dm$^3$.

Average annual indicator of ammonia nitrogen in the 3 tacson was on the level: 0.27±0.05 mg/dm$^3$, nitrites – 0.0069±0.0019 mg/dm$^3$, nitrites – 4.65±0.02 mg/dm$^3$. In some years of observation in the drinking water has been shown trend to increase nitrates in 2008: 6.96±0.33 mg/dm$^3$, i.e. (1.4 MAC); in 2013: 7.54±0.14 mg/dm$^3$, i.e. (1.5 MAC). Sometimes, nitrites decreased periodically in 2008 (6.96±0.33) mg/dm$^3$, and in 2014 (0.56±0.04) mg/dm$^3$ (p<0.001).

Drinking water sources in the 4 tacson characterized by unfavorable self-purification and incompleteness of nitrification activity for 7 – year period. Thus, in 2008 there were following levels: ammonia nitrogen (0.15±0.01) mg/dm$^3$; nitrites (0.039±0.014) mg/dm$^3$; nitrates (13.62±2.77) mg/dm$^3$ (p<0.001). In 2014 all these indicators decreased in the term of dynamics: ammonia nitrogen (0.12±0.01) mg/dm$^3$; nitrites (0.018±0.007) mg/dm$^3$; nitrates (11.48±4.09) mg/dm$^3$ (p<0.001), i.e. (1.25 MAC), (2.2 MAC), (1.2 MAC). It demonstrated significant trend to increase all these compounds in the drinking water: in 2008 – nitrites (2.0 MAC), nitrates (3.0 MAC); in 2009 – nitrates (5.5 MAC), nitrates (1.2 MAC); in 2011 – nitrates (3.4 MAC); in 2012 – nitrates (1.5 MAC); in 2014 – nitrates (2.3 MAC). Average annual indicators also increased: nitrites (1.4 MAC), nitrates (2.0 MAC), oxidation (6.0 MAC). On the other hand, level of ammonia nitrogen was permissible.

In 2014 indicators of nitrification activity was carried out on the level: (0.30±0.12) mg/dm$^3$ – ammonia nitrogen; (0.0016±0.0004) mg/dm$^3$ – nitrites; (11.57±0.03) mg/dm$^3$ – nitrates (p<0.001). Thereafter, there were determined increased of these parameters: nitrites (2.0 MAC) in 2008; (4.1 – 4.6 MAC) between 2010 and 2011; (1.05 MAC) in 2012; (2.0 MAC) – by average annual indicator.

Nitrates exceeded MAC all years of research: 2.7 times (in 2008); 1.3 – 1.1 times (between 2009 and 2010 years); 2.2 times (in 2011); 1.4 times (in 2012); 2.3 times (in 2014). The highest nitrates level was revealed in 2013: 47.45±6.33 mg/dm$^3$ (p<0.001), i.e. (10 MAC).

Results of our study in the 6 tacson decentralized water sources demonstrate good nitrification activity by low level of ammonia nitrogen and nitrites and high level of nitrates. So, in 2008, ammonia nitrogen significantly increased and was on the level: 0.58±0.02 mg/dm$^3$, nitrites – 0.10±0.009 mg/dm$^3$; nitrates – 6.09±0.25 mg/dm$^3$ (p<0.001). In 2014, ammonia nitrogen decreased 2.4 times and was on the level (0.24±0.05) mg/dm$^3$; nitrites – 3.5 times (0.029±0.008) mg/dm$^3$; nitrates increased 4.3 times (26.48±2.49) mg/dm$^3$. Ammonia nitrogen had never increase MAC, except in 2013: 0.37±0.08 mg/dm$^3$, i.e. (4.0 MAC).
Overnormal concentrations were carried out for nitrites in the drinking water sources in this tacson: between 2008 and 2009 years (5.0 – 4.0 MAC); between 2010 and 2011 years (6.5 – 7.5 MAC); in 2013 (3.6 MAC); in 2014 (1.45 MAC); average annual indicator was on the level (4.15 MAC).

Nitrites did not exceed MAC in the drinking water in 2012: (0.019±0.003) mg/dm$^3$ (p<0.001). On the other hand, nitrates exceeded MAC in the decentralized water supply sources during all years of observation, which should cause water born disease – methemoglobinemia among 6 tacson peasants. Thus, between 2008 and 2009 years, nitrates content was on the level (1.2 MAC); in 2010 (1.08 MAC); between 2011 and 2012 years (1.3 – 1.6 MAC); between 2013 and 2014 years (3.0 – 5.3 MAC); average annual indicator (2.08 MAC). It was shown the highest content of nitrates in the drinking water in 2014: (26.48±2.49) mg/dm$^3$ (Figure 2).

In the decentralized water sources pH was significantly increased (1.8 – 1.4) times in the 1 tacson; 1.1 times in terms of dynamics in the 2 tacson; 1.07 times in the 3 tacson (p<0.001). Content of pH in the 4 tacson was on the level (7.62±0.08) in 2008, thereafter decreased in 2014 (7.58±0.08). The greatest value of pH (7.62±0.08) was observed in the drinking water of 5 tacson in 2008. In the 6 tacson dynamics between 2008 and 2014 years have been shown increase of pH 1.1 times: from (6.71±0.18) to (7.64±0.12) (p<0.001).

Average annual concentrations of pH, ammonia nitrogen, nitrites and nitrates were varied in the different types of rural settlements, in the different water supply sources (Table 1).

Table 1. Chemical composition of drinking water in the centralized and decentralized sources of water-supply in the rural tacsons of Dnipropetrovsk region during (2008 - 2014) years.

<table>
<thead>
<tr>
<th>Type of rural tacson</th>
<th>Average annual indexes of drinking water quality (M±m)</th>
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<tbody>
<tr>
<td></td>
<td>pH</td>
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<tr>
<td>Centralized sources of water supply</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>7.54±0.11$^{1,2}$</td>
</tr>
<tr>
<td>2</td>
<td>7.5±0.09$^2$</td>
</tr>
<tr>
<td>3</td>
<td>7.45±0.04$^{1,2}$</td>
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<tr>
<td>4</td>
<td>7.55±0.03$^{1,2}$</td>
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<tr>
<td>5</td>
<td>7.35±0.03$^2$</td>
</tr>
<tr>
<td>6</td>
<td>7.40±0.04$^2$</td>
</tr>
<tr>
<td>Decentralized sources of water supply</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>8.33±0.65$^{1,2}$</td>
</tr>
<tr>
<td>2</td>
<td>7.27±0.15$^{1,2}$</td>
</tr>
<tr>
<td>3</td>
<td>7.52±0.09$^2$</td>
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<tr>
<td>4</td>
<td>7.53±0.05$^{1,2}$</td>
</tr>
<tr>
<td>5</td>
<td>7.26±0.09$^2$</td>
</tr>
<tr>
<td>6</td>
<td>7.22±0.10$^2$</td>
</tr>
</tbody>
</table>

Notes: $^1$ p – statistical significance level by $\chi^2$ – Pirson criterion; $^2$ p – by the Kruskall – Wallis analysis (p < 0.001); $^3$ p – by one factor analysis ANOVA (p < 0.05).
4. Conclusion

In the decentralized water supply sources all tascsons, except 6 tascson, had an unfavorable self-purification processes and incompletess of nitrification activity. It was proved that water from decentralized sources in the 1 – 5 tascsons of Dnipropetrovsk region did not correspond to the GOST 7525:2014 causerd by the high concentration of nitrites and nitrates between 2008 and 2014 year. Thus, according to the average annual indicators was identified high level of nitrites (42.5 MAC), nitrates (1.2 MAC) in the 1 tascson; (1.4 MAC) of nitrites and (2.0 MAC) of nitrates in the 4 tascson. Unfavorable nitrification activity in the decentralized drinking water sources in all tascsons of Dnipropetrovsk region, except 6 tascson, in 2008 – 2014 years was shown incompleteness of the self-purification water in the rural settlements, causing primary morbidity among peasants as well as the blood and blood – forming organs, methemoglobinemia among infants due to a consumption of water from wells.

In the centralized water supply sources of all tascsons was identified poor self-purification, as well as nitrogen ammonia decreased in dynamics for 2008 –2014 years, while nitrites and nitrates contents increased.

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