Tritium content as indicator of Cenomanian-Callovian groundwater complex state changes as a result of long-term operation within Kyiv city

*T. Koshliakova (M. P. Semenenko Institute of geochemistry, mineralogy and ore formation of the National Academy of Sciences of Ukraine), O. Koshliakov (Institute of Geology of Taras Shevchenko National University of Kyiv), O. Dyniak (Institute of Geology of Taras Shevchenko National University of Kyiv), I. Koshliakova (Institute of Geology of Taras Shevchenko National University of Kyiv)

SUMMARY

The paper considers the issue of changing the state of Cenomanian-Callovian groundwater complex. The studied groundwater complex is an important source of centralized and well-room potable water supply to Kyiv population, so the authors pay attention to study of hydrogeological changes of the complex state during long-term operation. The study confirms changes in water exchange structure, which are reflected in significant changes of Cenomanian-Callovian groundwater complex piezometric pressures surface and also in chemical state changes. In order to establish water exchange changes, a comparison of radioactive isotope hydrogen - tritium - content in investigated groundwater complex for 2014 and 2017 was performed. Mathematical-statistical methods were used to establish changes. The obtained results indicate that during 2014-2017 the chemical state of Cenomanian-Callovian groundwater complex in terms of tritium content as a whole changed. Since 2008, due to groundwater production reduction, there has been a recovery of groundwater levels and a positive trend of changes in chemical state of investigated groundwater complex in the direction of its gradual return to its natural state.
Introduction

Since the end of the XIX century Cenomanian-Callovian groundwater complex is an important source of centralized and well-room potable water supply within Kyiv city, so the study of hydrogeological changes of the complex during long-term operation has a great importance. Investigated groundwater complex is more isolated from external recharge sources in comparison with the aquifer of Kaniv and Buchach Eocene sediments. Therefore, Cenomanian-Callovian groundwater complex operation leads to the formation of larger and deeper depression funnels and corresponding difference in piezometric pressures. The latter provides more active downward filtration through low permeability deposits of cretaceous-marl layer of the Upper Cretaceous in such areas. In turn, water exchange restructuring in the aquifer of Kaniv and Buchach Eocene sediments and Cenomanian-Callovian groundwater complex also led to anthropogenic changes in cretaceous-marl layer of the Upper Cretaceous that separates them.

Thus, as of 1988 (Shestopalov et al., 1988), due to the long-term operation of Cenomanian-Callovian groundwater complex within Kyiv territory, significant changes in water exchange structure have taken place. Within the river valleys in the areas of groundwater intakes, the most significant inversion of the flow was recorded: zones of natural upward filtration turned in places into areas of active downward filtration. It was also noted the intensification of downward filtration. The structure of lateral filtration of investigated groundwater complex has changed significantly, the speed of which has increased by an average of 1.5 times compared to natural.

Method and Theory

According to the authors' own research, the above changes in water exchange structure were reflected in substantive changes in piezometric pressures surface of Cenomanian-Callovian groundwater complex, which is illustrated by schematic maps of piezometric levels as of 1960 and 2005 (Koshliakova et al., 2015). As of 2010, a general tendency to water quality class deterioration of investigated groundwater complex within Kyiv was revealed and it was also established that changes in major chemical composition components, the same as of piezometric levels changes, are uneven in area and depend on the intensity of operation (Koshliakova and Koshliakov, 2014). That is, as of 2005-2010, there was a general trend of Cenomanian-Callovian groundwater complex ecological conditions deterioration, the main factor of which is the long-term groundwater exploitation.

But the results of geological and economic reassessment of Kyiv potable groundwater field operational reserves, performed in 2017 (Fedorenko et al., 2017), indicate the following. Compared to previous Kyiv territory hydrogeological study period in 1972 (Litvak et al., 1972) groundwater production from Cenomanian-Callovian groundwater complex after 2008 decreased significantly (approximately decreased by 4 times), and the piezometric surface increased by approximately 10.0-20.0 m. That is, in recent years, due groundwater production reduction, there is a rapid recovery of the levels of the studied groundwater complex. It follows that lately Cenomanian-Callovian groundwater complex state is gradually returning to natural.

If this is the case, it should lately also be a positive trend of groundwater chemical conditions changes towards its return to its natural state. First of all, it should be manifested in uneven distribution decrease of chemical components over the area. Therefore, a comparison of radioactive isotope hydrogen – tritium – content in Cenomanian-Callovian groundwater complex for 2014 and 2017 was performed. From the city's well-rooms developed for investigated groundwater complex 157 samples were taken (77 samples in 2014 and 80 samples in 2017) and the tritium content in water was determined (Figure 1). Chemical analyzes to detect the tritium content in water samples were performed at the State Institution "Institute of Environmental Geochemistry of the National Academy of Sciences of Ukraine".
Results

For comparative assessment, statistical processing of the obtained data was performed. Since investigated groundwater complex is characterized by homogeneous geological structure within the city, and the well-rooms are located statistically evenly and randomly, the authors used a of random variable model.

![Figure 1: Tritium content in Kyiv well-rooms as of 2014 and 2017](image)

The results of tritium determination for 2014 and 2017 were considered as separate statistical samples. The following values were calculated for each of them: arithmetic mean, standard deviation, asymmetry and excess coefficients. The results are shown in Table 1.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>The results of statistical values calculations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Year</td>
<td>Number of values</td>
</tr>
<tr>
<td>2014</td>
<td>77</td>
</tr>
<tr>
<td>2017</td>
<td>80</td>
</tr>
</tbody>
</table>

As a result of testing the hypothesis that the sample distributions correspond to the normal distribution law using the "three sigma" rule, it was found that with a probability of 0,99 it cannot be said that the
sample distributions do not obey the normal law. Therefore, the authors accepted the hypothesis of the normality of tritium content distribution for both samples.

Next, we tested the hypothesis that these samples belong to one general population using analysis of dispersion (Fisher's F-test was used) and comparison of arithmetic means (Student's t-test). Assuming that during 2014-2017 chemical conditions of Cenomanian-Callovian groundwater complex as a whole has not changed, the samples will belong to one general population. In the case of significant changes in water chemical composition, tritium content samples will not belong to one general population. Table 2 shows the results of Fisher's F-statistics and Student's t-statistics calculations for samples comparison.

**Table 2 The results of Fisher's F-statistics and Student's t-statistics calculations**

<table>
<thead>
<tr>
<th>Year</th>
<th>Number of values</th>
<th>Dispersion, (Bq/dm³)²</th>
<th>Arithmetic mean, Bq/dm³</th>
<th>Fisher's F-statistics</th>
<th>Student's t-statistics</th>
</tr>
</thead>
<tbody>
<tr>
<td>2014</td>
<td>77</td>
<td>3,049</td>
<td>5,61</td>
<td>1,601</td>
<td>0,848</td>
</tr>
<tr>
<td>2017</td>
<td>80</td>
<td>1,943</td>
<td>5,50</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Analysis of the results presented in Table 2 shows that the samples do not belong to one general population, because their dispersions are different. Therefore, it can be argued that during 2014-2017, the chemical state of Cenomanian-Callovian groundwater complex in terms of tritium content as a whole has changed. Dispersion decrease of the sample in 2017 compared to 2014 indicates that there is a decrease in the uneven distribution of tritium over the area against the background of a constant average value. This suggests that lately there has been a positive trend of changes in investigated groundwater complex chemical state in the direction of its gradual return to its natural state.

**Conclusions**

Until 2005-2010, the general trend of deterioration of Cenomanian-Callovian groundwater complex ecological condition persisted, the main factor of which was long-term intensive groundwater production.

Since 2008, due to groundwater production reduction, the levels of studied groundwater complex have been restored, and its piezometric surface has already increased by approximately 10,0-20,0 m.

A comparison of the results of tritium content determining in investigated groundwater in 2014 and 2017 showed that there is a decrease in the uneven distribution of tritium content over the area against the background of a constant average value. Thus, there is a positive trend of changes in the groundwater chemical state towards its return to its natural state.

Eventually, it can be argued that in recent years hydrogeological changes in Cenomanian-Callovian groundwater complex state are positive, and groundwater conditions returning to natural.

**References**


