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# POTABLE CENOMANIAN-CALLOVIAN GROUNDWATER COMPLEX CHEMICAL COMPOSITION CHANGES DYNAMICS IN KYIV AS A RESULT OF LONG-TERM EXPLOITATION

*(Reviewed by the editorial board member M. Korjnev)*

***Purpose.*** *Potable ground water chemical composition and quality class changes tendencies of Cenomanian-Callovian groundwater complex in Kyiv as a result of long-term exploitation were revealed. For this purpose mathematical-statistical methods and GIS-technologies were used.*

***Methodology.*** *In the research systemic, mathematical-statistical, geoinformational approaches, typification method and descriptive procedure were used. For mathematical and statistical processing Microsoft Excel, Statistica, Attestat software packages were chosen; for cartographic schemes construction and for spatial analysis and modelling in GIS Corel Draw, MapInfo Professional and ArcView programs were used.*

***Findings.*** *Kyiv potable ground water chemical composition and quality class changes investigation methodology on the basis of combined mathematical-statistical methods and geoinformatics technologies were developed. Non-parametric statistics method (Mann-Witney criterion), used for hydrogeochemistry data analysis, description and substantiation are given. Kyiv territory typification, based on geomorphology characteristic, was done; the most vulnerable to contamination city zones were defined.*

***Originality.*** *For the first time general tendency of Cenomanian-Callovian groundwater complex deterioration was revealed in Kyiv; it was determined that city potable groundwater chemical composition basic components changes of observable groundwater complex have irregular space character and depend on exploitation intension and geo-hydrogeological and geomorphological territory district structure. Also for the first time Kyiv territory typification, based on Cenomanian-Callovian potable ground water chemical composition basic components and quality class changes, was implemented; deterioration tendencies were determined.*

***Practical value.*** *Practical application of determined Cenomanian-Callovian complex potable ground water chemical composition and quality class changes tendencies in Kyiv will allow to prevent further ground water deterioration with the help of exploitation system optimization. Obtained results have the potential to become the basis for the potable ground water chemical composition monitoring system development in Kyiv; methodological approaches and techniques can be used for urbanized territories ground water study.*

**Introduction.** Nowadays Kyiv population potable water supply is provided both at the expense of surface water (75,9 % of city supply general balance) and groundwater (24,1 %) [5]. Since surface waters are polluted and need considerable preliminary water preparation for potable quality assurance, strategically important potable water source is groundwater. From this point of view within the bounds of Kyiv important groundwater sourses are groundwater complex in sediments of the middle and the upper Jurassic Ivanytska formation and the lower and the upper Cretaceous Zagoryvska, Zhuravynska, Burimska formation (next – Cenomanian-Callovian groundwater complex) and aquifer in sediments of the middle Jurassic Bayos layer Orelska formation.

During long-term exploitation (more than 100 years), significant changes of active water exchange zone hydrodynamic conditions appeared. Also these changes are detected in the above mentioned groundwater complex and aquifer [2, 4]. This potentially should have an effect on groundwater chemical composition. However, modern water quality observation system is exceptionally factographic (MPC accordance periodical dotted control) and doesn't provide spatio-temporal estimation of groundwater chemical composition changes, the same way as deterioration forecasting.

In this connection the necessity of research to reveal potable Cenomanian-Callovian groundwater complex chemical composition and quality changes tendencies, based on modern native and european requirements, appeared.

**Methodology.** Systemic, mathematical-statistical, geoinformational approaches, typification method and descriptive procedure were used in research. For mathematical and statistical processing Microsoft Excel, Statistica, Attestat software packages were chosen; for cartographic schemes construction and for spatial analysis and modelling in GIS Corel Draw, MapInfo Professional and ArcView programs were used.

Accumulated during decades data about chemical composition of Cenomanian-Callovian groundwater complex are disordered on area and in time. For the purpose to generalizate this data in the view of spatio-temporal estimation of water quality changes, the author has created geoinformational database model with the help of MapInfo Professional software (scale 1:10000, projection GK, zone 6, Pulkovo 1942). The attributive table architecture, containing Cenomanian-Callovian groundwater complex chemical composition and bacteriological quality factors on separate wells, has been designed. The table contains both modern and archival data. Today geoinformational database model supports information on 298 wells.

Given data have been analyzed by using the demands of National Standard of Ukraine "Sources of centrical potable water-supply. Hygienic and ecological demands for water quality and withdrawal principles. ДСТУ 4808:2007" [6]. These demands are designed for the centrical potable water-supply sources and determine hygienic, ecological and technological requirements for new and present centrical water-supply sources.

It has been revealed that, during long-term exploitation, Cenomanian-Callovian groundwater complex quality has become worse in such factors as mineralization (has changed from 1 quality class to 3 class) and hardness (has changed from 3 quality class to 4 class).

For such groundwater chemical composition factors as mineralization, ammonium and oxidizability histograms have been constructed and verification of samples in accordance to normal (logarithmically normal) probability law has been done (Figure 1).

It has been revealed that different temporal samples obey different statistical laws (normal or logarithmically normal). In many cases is not possible to determine statistical law. Bimodal distribution existence for oxidizability gives the possibility to assume that this factor changes on area irregularly. At the next research stage for each factor verification of two different temporal samples (the end of the XIX – the beginning of the XX century and the beginning of the XXI century) accordance to the one universal set by means of Mann-Witney criterion has been done [1].

The following statistically significant results have been obtained. Longstanding monitoring data show that mineralization value (mean and median) in Cenomanian-

Callovian groundwater complex has practically not changed (mean 356,9 ppm and median 350 ppm at the beginning of the XXI century compared to mean 356,5 ppm and median 353,7 ppm at the end of the XIX – the beginning of the XX century). As for ammonium concentration in observable groundwater complex, its value has been stable till the 1990s, when ammonium mean value rose to 1,3 ppm and median value rose to 0,4 ppm. At the beginning of the XXI century ammonium concentration decreased to the end of the XIX century – the beginning of the XX century level. Oxidizability concentration rose in mean value in 1,38 ppm and in median value in 0,87 ppm at the groundwater complex intensive exploitation period (the 1960s-1980s). Though statistically in oxidizability today's Cenomanian-Callovian chemical composition does not differ from the end of the XIX – the beginning of the XX century, mean and median oxidizability values in the 2000s are higher than at the beginning of exploitation.

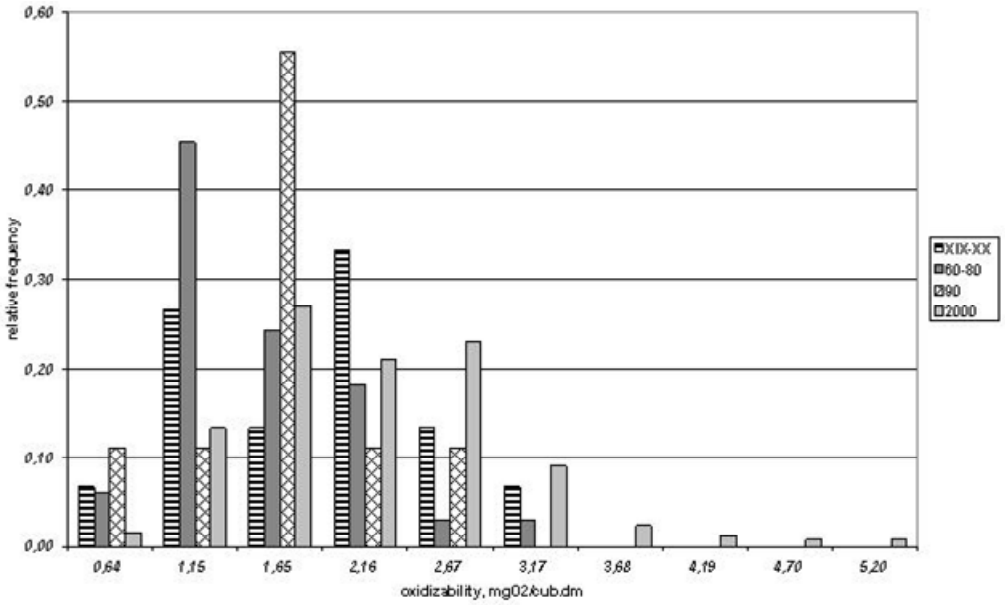


**Figure 1. Oxidizability value histogram for period from the end of the XIX to the beginning of the XXI century**

The author has suggested that irregularity of Cenomanian-Callovian groundwater complex chemical composition factors changes are stipulated by the territory geological-hydrogeological and geomorphological structure features and long-term groundwater complex exploitation. With the aim to check this suggestion the author has constructed five schematic geological-hydrogeological sections for the Kyiv territory districts, which geomorphologically differ from each other, on the basis of available printed and fund materials: Prydniprovska upland flat part, Prydniprovska upland loess residual outcrops, minor rivers valleys, the Dnipro river valley and the part of Prydniprovska lowland. The main aquifers and groundwater complexes hydrodynamic heads as of the middle of the XX century and of the beginning of the XXI century have been put on sections. Constructed sections testify that territory districts are characterized by difference in inter-relations of the main aquifers and groundwater complexes hydrodynamic heads. Therefore the conclusion was drawn about necessity of further research taking into account the above mentioned territory typification. For this purpose geoinformational database model in MapInfo Professional software has been amplified with respective layer which spatially reflects such typification (Figure 2).

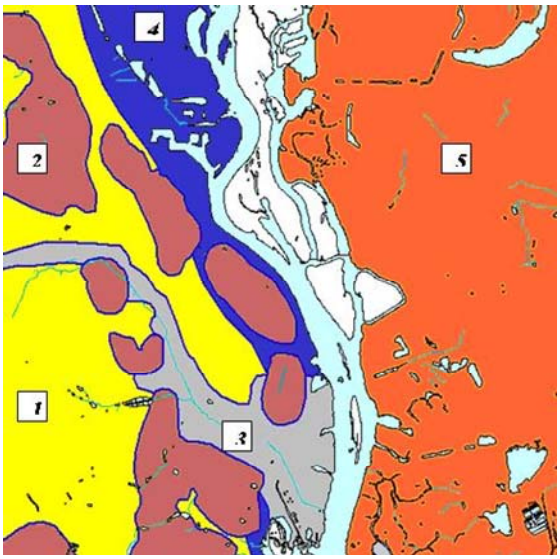


**Figure 2. Geoinformational layer of Kyiv with territory typification:**
1 – Prydniprovska upland flat part; 2 – Prydniprovska upland loess residual outcrops; 3 – minor rivers valleys;
4 – the Dnipro river valley; 5 – the part of Prydniprovska lowland

Groundwater chemical analyses results samples have been formed separately for each type with the aim of further mathematical-statistical treatment. By means of Statistica software using non-parametric Mann-Witney criterion verification of samples belonging to the one universal set has been done for four time periods: the end of the XIX – the beginning of the XX century, the 1960s-1980s, the 1990s, the beginning of the XXI century. Different temporal samples of selected factors have been compared both for each separate territory type and for different types [3].

It has been revealed that within the limits of Prydniprovska upland flat part and Prydniprovska upland loess residual outcrops, minor rivers valleys and the part of Prydniprovska lowland mineralization stays invariable during all the groundwater complex exploitation period. However within the limits of the Dnipro river valley mineralization has decreased since the 1990s and stays this way today.

Within the bounds of Prydniprovska upland loess residual outcrops and minor rivers valleys ammonium does not change. In Prydniprovska upland flat part and the Dnipro river valley ammonium concentration decreased in the 1960s-1980s. Next within the limits of the Dnipro river valley changes are not fixed, while in Prydniprovska upland flat part ammonium value increased in the 1990s; at the beginning of the XXI century ammonium decreased again.

Within the limits of Prydniprovska upland loess residual outcrops, the Dnipro river valley, minor rivers valleys oxidizability value increased at the groundwater complex intensive exploitation period (the 1960s-1980s) and stays this way today. However in Prydniprovska upland flat part oxidizability value remained stable before the beginning of the XXI century. Today oxidizability has decreased compared to the 1990s of the XX century.

During the research of groundwater complex chemical composition changes process between isolated territory types the following tendencies have been revealed:

1. The highest mineralization values at the end of the XIX century – the beginning of the XX century were within the limits of the Dnipro river valley (median 388,4 ppm). In mineralization the Dnipro river valley has exceeded Prydniprovska upland flat part (332 ppm), minor rivers valleys (348 ppm) and Prydniprovska upland loess residual outcrops (328 ppm). In the 1960s-1980s mineralization values in all five types became uniform and stay this way.

2. The highest oxidizability values at the end of the XIX century – the beginning of the XX century were within the limits of Prydniprovska upland loess residual outcrops (1,6 ppm) which exceeded Prydniprovska upland flat part (1,25 ppm) and minor rivers valleys (1,36 ppm). In the 1960s-1980s of the XX century oxidizability values increased in the Dnipro river valley and essentially exceeded Prydniprovska upland flat part and the part of Prydniprovska lowland. The highest oxidizability values at the beginning of the XXI century are in the part of Prydniprovska lowland (2,23 ppm) which exceed Prydniprovska upland flat part (1,84 ppm) and the Dnipro river valley (1,64 ppm).

3. At the end of the XIX century – the beginning of the XX century ammonium values were different in all the types: the lowest values were in Prydniprovska upland loess residual outcrops (0,28 ppm) and in minor rivers valleys (0,15 ppm). The highest ammonium values were in Prydniprovska upland flat part (0,36 ppm) and the Dnipro river valley (0,35 ppm). In the 1960s-1980s ammonium values in all five types became uniform and remained this way before the beginning of the XXI century. The highest ammonium values at the beginning of the XXI century are within the limits of minor rivers valleys (0,42 ppm) and in the Dnipro river valley (0,38 ppm), which exceed Prydniprovska upland flat part (0,14 ppm) and Prydniprovska upland loess residual outcrops (0,22 ppm).

**Conclusions.** It is possible to contend that the most vulnerable to groundwater chemical composition changes territory types are minor rivers valleys, the Dnipro river valley and the part of Prydniprovska lowland. These three types are characterized by increasing of mineralization, ammonium and oxidizability values in time. This phenomenon can be explained by the fact that the above mentioned types are geologically less protected from surface contamination. Moreover, these types are more influenced by surface water than other types. Cenomanian-Callovian groundwater complex chemical balance disturbance contemporizes with hydrodynamic conditions disturbance, determined by experts-hydrogeologists since the 1950s.

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## ДИНАМІКА ЗМІН ХІМІЧНОГО СКЛАДУ ПИТНИХ ПІДЗЕМНИХ ВОД СЕНОМАН-КЕЛОВЕЙСЬКОГО ВОДОНОСНОГО КОМПЛЕКСУ НА ТЕРИТОРІЇ м. КИЄВА В УМОВАХ ТРИВАЛОЇ ЕКСПЛУАТАЦІЇ

***Мета.*** *Виявлення тенденцій змін хімічного складу та класу якості питних підземних вод сеноман-келовейського водоносного комплексу в межах м. Києва, викликаних тривалою експлуатацією, за допомогою математико-статистичних методів та ГІС-технологій.*

***Методика.*** *В роботі застосовані системний, математико-статистичний, геоінформаційний підходи до вивчення об'єкта, метод типізації та описовий метод. Для математичної і статистичної обробки були обрані пакети програм Microsoft Excel, Statistica, Attestat; для побудови картографічних схем, а також для просторового аналізу і моделювання в ГІС були застосовані програми Corel Draw, MapInfo Professional та ArcView.*

***Результати.*** *Розроблена методика дослідження змін хімічного складу та якості питних підземних вод м. Києва на базі спільного застосування методів математичної статистики та геоінформаційних технологій. Наведено опис та обґрунтування застосування методів непараметричної статистики (критерій Мана-Уітні), що був використаний для аналізу гідрохімічних даних. Виконана типізація території м. Києва та виділені найбільш вразливі до забруднення ділянки міста.*

***Наукова новизна.*** *Вперше виявлена загальна тенденція до погіршення класу якості води сеноман-келовейського водоносного комплексу в межах території м. Києва. Встановлено, що зміни основних компонентів хімічного складу питних підземних вод досліджуваного водоносного комплексу на території міста мають нерівномірний за площею характер і залежать від інтенсивності експлуатації та геолого-гідрогеологічної і геоморфологічної будови ділянки території. Також вперше була виконана типізація території м. Києва за змінами основних компонентів хімічного складу та класу якості питних підземних вод сеноман-келовейського водоносного комплексу і встановлені тенденції цих змін.*

***Практична значимість.*** *Практичне врахування встановлених тенденцій змін хімічного складу та класу якості питних підземних вод сеноман-келовейского водоносного комплексу в межах м. Києва дозволить запобігти подальшому погіршенню якості підземних вод шляхом оптимізації системи їх експлуатації. Отримані результати можуть слугувати основою для розробки системи моніторингу хімічного складу питних підземних вод у м. Києві, методичні підходи та прийоми можуть бути використані для вивчення підземних вод на інших урбанізованих територіях.*

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## ДИНАМИКА ИЗМЕНЕНИЙ ХИМИЧЕСКОГО СОСТАВА ПИТЬЕВЫХ ПОДЗЕМНЫХ ВОД СЕНОМАН-КЕЛОВЕЙСКОГО ВОДОНОСНОГО КОМПЛЕКСА НА ТЕРРИТОРИИ г. КИЕВА В УСЛОВИЯХ ДЛИТЕЛЬНОЙ ЭКСПЛУАТАЦИИ

***Цель.*** *Выявление тенденций изменений химического состава и класса качества питьевых подземных вод сеноман-келловейского водоносного комплекса в пределах города Киева, вызванных длительной эксплуатацией, при помощи математико-статистических методов и ГИС-технологий.*

***Методика.*** *В работе использованы системный, математико-статистический, геоинформационный подходы к изучению объекта, метод типизации и описательный метод. Для математической и статистической обработки были выбраны пакеты программ Microsoft Excel, Statistica, Attestat; для построения картографических схем, а также для пространственного анализа и моделирования в ГИС были использованы программы Corel Draw, MapInfo Professional и ArcView.*

***Результаты.*** *Предлагается методика исследования изменений химического состава и качества питьевых подземных вод г. Киева на базе совместного применения методов математической статистики и геоинформационных технологий. Приведено описание и обоснование методов непараметрической статистики (критерий Манна-Уитни) и критерия Аббе, которые были использованы для анализа гидрохимических данных. Выполнена типизация территории г. Киева по геоморфологическому признаку и выделены наиболее уязвимые к загрязнению участки города.*

***Научная новизна.*** *Впервые выявлена общая тенденция к ухудшению класса качества воды сеноман-келловейского водоносного комплекса в пределах территории г. Киева и установлено, что изменения основных компонентов химического состава питьевых подземных вод исследуемого водоносного комплекса на территории города имеют неравномерный по площади характер и зависят от интенсивности эксплуатации, а также геолого-гидрогеологического и геоморфологического строения участка территории. Также впервые была выполнена типизация территории г. Киева по изменениям основных компонентов химического состава и класса качества питьевых подземных вод сеноман-келловейского водоносного комплекса и установлены тенденции этих изменений.*

***Практическая значимость.*** *Практический учет установленых тенденций изменений химического состава и класса качества питьевых подземных вод сеноман-келловейского водоносного комплекса в пределах г. Киева позволит предотвратить дальнейшее ухудшение качества подземных вод путем оптимизации системы их эксплуатации. Полученные результаты могут послужить основой для разработки системы мониторинга химического состава питьевых подземных вод в г. Киеве, методические подходы и приемы могут быть использованы для изучения подземных вод на урбанизированных территориях.*