ORIGINAL ARTICLE

Ecological and geochemical aspects of interlayer water use for potable water supply of urban population: a case study in the Dnieper–Donetsk aquifer system, Ukraine

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Abstract The article is devoted to the study of ecological and geochemical features of interlayer waters of the Dnieper-Donetsk aquifer system in Ukraine, used for the potable water supply of Kyiv. A wide range of methods was used, including Microsoft Excel, Statistica, and Attestat software packages, MapInfo Professional 6.5 and ArcGIS-ArcMap 9.3 programs; the method of mass spectrometry with inductively coupled plasma (ICP-MS) and GEMS software were performed. Monitoring study results (during 2007-2023) were analyzed for two interlayer aquifers-Cenomanian-Callovian groundwater complex and Bajocian aquifer. It was determined that the normalized value of mineralization increased with a decrease in water intake during 1980-2010, which indicates a relative increase in the content of mineral substances during longterm exploitation. A high negative correlation (Kcor. = -0.54 to -0.86) is also typical for normalized values of oxidizability, total hardness, pH, Ca, Mg, and Cl content. Comparative analysis of two different aquifers revealed that the macrocomponent composition of Bajocian aquifer remains stable, once for Cenomanian-Callovian groundwater complex, there is a tendency to decrease hydrogen carbonates and increase chlorides and sulfates, whereas the

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¹ M.P. Semenenko Institute of Geochemistry, Mineralogy and Ore Formation of the NAS of Ukraine, 34, Acad. Palladin Ave., Kyiv 03142, Ukraine cation composition remains relatively stable. A significant increase (by 55%) of the total mineralization in the representative well located on the right bank of the Dnieper River was found. There is also a significant increase (by more than 5 times) in the iron content, which the authors associate with the unsatisfactory technical condition of the well casing pipes. Physico-chemical modeling of trace elements, performed for investigated aquifers, shows that both aquifers are characterized by the predominant migration of the following metals in the cationic form (aqua-ions): Ca, Mg, Na, Ba, Co, Cu, Mn, Ni, Sr, Zn. It was found that the predominant migration forms of metals in the studied interlayer waters are free uncomplexed ions, carbonate, and hydroxo complexes.

Keywords Interlayer water · Hydrogeochemistry · Environmental geochemistry · Microelements · Migration forms · Biologically significant concentrations

Abbreviations

UN	United Nations
AS	Aquifer system
ICP-	Mass spectrometry with inductively coupled
MS	plasma
MPC	Maximum permissible concentration
BSC	Biologically significant concentration
LLBSC	Lower limit of biologically significant
	concentration
USEPA	United States Environmental Protection Agency
EU	European Union

1 Introduction

Most of the Earth's liquid freshwater is found, not in lakes and rivers, but is stored underground in aquifers. These aquifers provide a valuable baseflow supplying water to rivers during periods of no rainfall. They are therefore an essential resource that requires protection so that groundwater can continue to sustain the human race and the various ecosystems that depend on it. The last 50 years have seen an unprecedented development of groundwater resources. Globally, groundwater use is enormous, but it is generally recognized that the extent of its use tends to be underestimated, not least because the very ease and ubiquity of groundwater development means that much vital small-scale use is excluded from official statistics. At a regional level, groundwater is of huge importance in Africa, Asia, and Central and South America. Nationally, countries from Palestine to Denmark are dependent on groundwater and examples of local reliance can be drawn from Mexico City to small villages in Ethiopia. According to the UN, as of 2000, an estimated 2 billion people worldwide rely on aquifers for a drinking water supply. Moreover, 40% of the world's food is produced by irrigated agriculture that relies largely on groundwater. In the future, aquifer development will continue to be fundamental to economic development and reliable water supplies will be needed for domestic, industrial, and irrigation purposes (Morris et al. 2003; Misstear et al. 2022).

Ukraine belongs to the countries poorly provided with water resources (about 1500 m^3 /year per inhabitant, while the UN considers this figure to be sufficient at the level of 10–15 thousand m^3 /year).

Groundwater (specially interlayer), which is protected from above pollution, serves as a strategic source for Ukrainian cities' population because in some emergencies becomes the only reliable source of potable water supply. To successfully solve this problem, it is necessary to study the regularities of groundwater resource formation, and the influence of man-made and natural factors on their changes (Rudenko et al. 2021).

Environmental geochemistry, in particular hydrogeochemistry, is an essential modern scientific direction that is actively developing all over the world (Sracek and Hirata 2002; Golekar et al. 2013; Hussain et al. 2019; Paternoster et al. 2021; Eftimi and Sara 2022). This scientific direction aims to study the microelement composition of natural solutions (groundwater) in terms of connection with human health. This enables the assessment of the stability and reliability of deep artesian aquifers (including interlayer water) as a strategic source for providing the urban population with safe and pure potable water (Levoniuk and Udalov 2022).

2 Factors forming the groundwater chemical composition and elements migration

The problem of forming the groundwater chemical composition is one of the most important in hydrogeology. Chemistry is the result of a complex interaction of the natural system components (rocks-gases-organic matter) during the long-term geological development of a particular region. Therefore, the modern chemical composition of groundwater is, to some extent, an imprint of its geological history. Its formation is related to factors and processes occurring in the Earth's crust. Among them, endogenous and exogenous are distinguished. Exogenous factors, in turn, are divided into natural and artificial (anthropogenic). The most essential factors in forming the groundwater chemical composition are: physical and geographical (climate, topography, hydrology, amount of atmospheric precipitation etc.); geological (lithological composition of rocks, tectonic movements, magmatism, geothermal and gas regimes of the subsoil, etc.); hydrogeological (groundwater dynamics, fractured water-bearing rocks, filtration rate, etc.); physical and chemical (chemical properties of elements, the solubility of chemical compounds, forms of elements migration, pH and Eh of water environment, radiolysis, cation exchange, temperature, pressure); biological (influence of living matter); anthropogenic. A group of geological factors constantly regulate changes in thermodynamic and physicochemical balance in hydrogeological systems. This has the biggest influence on groundwater chemical composition. The litho-facies composition of water-bearing rocks is a leading factor in the formation of background waters in the upper hydrogeodynamic zones. It defines the processes of cation exchange, leaching, and dissolution of minerals and rocks, as a result of which groundwater is mostly enriched with the main macrocomponents, microelements, and gases. In deep hydrogeological structures, rocks are intensively displaced by discontinuous tectonic disturbances. In such conditions, the influence of the lithologic-facies composition of waterbearing rocks decreases due to the increasing importance of deep heat and mass transfer in the groundwater chemical composition formation. The significance of a given process in the chemical composition formation is determined by the depth of aquifers and groundwater complexes. The tectonics of hydrogeological structures, the degree of hydrodynamic openness, and ultimately the mass transfer intensity in the underground hydrosphere have a great influence (Bezruk et al. 2013).

Groundwater quality is a sensitive issue that transcends national borders. Currently, the assessment of possible interactions in the "water–rock" system of the aquifer is widely used in hydrogeological works both to assess the direction of the evolution of the water composition and to determine their suitability for consumption and agricultural use. Statistical methods and the complex use of balance methods, various types of diagrams, as well as the geochemical (thermodynamic) modeling method are used to perform such assessments (Koliabina et al. 2021).

Geochemical features of the migration of chemical elements, especially heavy metals, in the underground hydrosphere are extremely complex and diverse. The peculiarities of their behavior are determined by a wide range of factors, both natural and man-made. The main factors include the forms of concentration of chemical elements in the solid phase of water-bearing rocks, solubility of minerals, and geochemically significant forms of migration of elements in natural waters.

Currently, knowledge of the background content of microelements, and their spatial distribution in potable artesian waters of large urban agglomerations has not only a purely scientific, but also a social significance. Learning of its impact on the population's health will help to develop measures to improve the ecological situation and prevent the emergence of unwanted diseases, i.e., trace element diseases associated with a lack or excess of chemical elements entering the trophic chain (Zlobina 2013). These main points determine the relevance of the presented study.

3 Research area

3.1 Modern hydrogeological zoning of Ukraine

A total of 10 first-order aquifer systems (AS) have been identified on the territory of Ukraine, which is characterized by certain features of the geological and hydrogeological cross-section of rocks and regional regularities of hydrogeological conditions: Transcarpathian AS, Carpathian AS, Precarpathian AS, AS of Ukrainian Shield, Volyn-Podillya AS, Dnieper–Donetsk AS, Donbas AS, the Black Sea AS, the North Dobruja AS, and AS of Mountain Crimea (Shestopalov et al. 2019).

The object of the presented study is the Dnieper– Donetsk AS, a vivid example of a classic artesian basin. This hydrogeological structure is located in the northeastern part of Ukraine within the Dnieper–Donetsk depression and covers the territories of the Chernihiv region, Sumy region, Poltava region, Kharkiv region (without the southeastern part), and the northern parts of the Kyiv region, Cherkasy region, and Luhansk region (Fig. 1).

3.2 The Dnieper–Donetsk aquifer system

The Dnieper-Donetsk AS is the largest hydrogeological structure in Ukraine. The surface system of aquifers and complexes, that determine its hydrogeological conditions includes 40% of all Ukrainian groundwater operational resources. It is a classic type of artesian basin characterized by the persistence of aquifers and layers that spread over large areas. This AS is characterized by the superficial nature of the aquifer's occurrence. The layer of sedimentary rocks is saturated with groundwater and serves the unified water-bearing system of the aquifers, which are interlinked and connected with surface waters to varying degrees through poorly permeable layers of rocks. The thickness of the zone of intensive water exchange ranges from 300 to 700 m. Kyiv groundwater deposit is typical for the northwestern slope of the Dnieper-Donetsk AS. The regional poorly permeable layers common within this deposit contribute to a decrease in the intensity of vertical water exchange with depth, it is much higher in the upper aquifers and complexes than in the lower ones. The same aquifer receives a maximum supply on the sides of the aquifer structure (the border with the Ukrainian shield) and a minimum, in the central, most submerged part (due to the increase in thickness and the deterioration of the filtration properties of the separate layers) (Kuraieva et al. 2020).

3.3 Kyiv industrial urban agglomeration

The capital of Ukraine, Kyiv, is a traditional consumer of groundwater (from the beginning of the exploitation of deep artesian aquifers to the second half of the nineteenth century). Currently, the centralized water supply is provided by 48.8% of the water from the Desna River, 27.1% from the Dnieper River, and 24.1% from underground sources. In addition, to provide the population with pure potable water, a network of pumping stations (174 wells in total) has been installed on the city's territory. From the point of view of potable water supply within the city of Kyiv, interlayer aquifers are strategically important: (1) groundwater complex in the deposits of Ivanytska formation of the Middle and Upper Jurassic and Zahorivska, Zhuravynska, and Buromska formations of the Lower and Upper Cretaceous $(J_{2-3}iv + K_{1-2}zg-br)$ —further in the text-Cenomanian-Callovian groundwater complex, timed to sands, sandstones with layers of limestone, flint, clay, siltstone, and marl; (2) aquifer in the deposits of Orelska formation of the Middle Jurassic (J₂or)-further in the text-Bajocian aquifer, timed to variegated sand with clay layers and brown coal lenses. It is worth noting that currently only 47% of the approved operational reserves of the Kyiv deposit groundwaters are used (Koshliakova 2015).



Fig. 1 Location of the Dnieper–Donetsk aquifer system in Ukraine. Schematic map. Large cyrillic letters mark the indexes of Ukrainian aquifer systems

Kyiv industrial urban agglomeration has a complex geological and hydrogeological structure with specific features of the distribution of filtration parameters of aquifers, complex interconnections of adjacent aquifers, the heterogeneous chemical composition of groundwater, disturbances of level and hydrochemical regimes (Rudenko et al. 2021). On the city's territory, a system of surfacelying aquifers and complexes and poorly permeable layers (imperfect confining beds) is spread, complicated by "hydrogeological windows" and significant tectonic disturbances inherited in the cross-section of loose sediments in the Dnieper River valley. Furthermore, there are preferential zones associated with depression forms of the microlandscape. The total thickness of the aquifer system is 400 m (Koshliakova 2015).

Kyiv's groundwater deposit serves as a clear example of a hydrogeological object that has been affected by a complex of anthropogenic factors for a long time (over 100 years). The emergence of new sources of water exchange formation (water intakes, reclamation systems, hydro-technical structures) determined the change in the structure and intensity of water exchange both between groundwater complexes (aquifers), and underground and surface waters. Intensive exploitation of groundwater caused the development of a regional depression funnel in the Bajocian aquifer and local ones (practically equal in area to the urban territory of Kyiv) in the Cenomanian-Callovian groundwater complex. There has been an intensification (sometimes by an order of magnitude or more) of water flow between aquifers and complexes. Such processes cause concern, because, although the Cenomanian-Callovian groundwater complex and Bajocian aquifer are located at a considerable depth (90-200 m) and are considered protected (conditionally protected on the left bank of the Dnieper river) from pollution, some studies in recent years (Koshliakova 2015; Zlobina 2013) evidenced man-made changes in the chemical composition of groundwater, in particular, quality deterioration: an increase in the amount of mineralization, hardness, the concentration of chlorides, ammonium, and oxidizability in Cenomanian-Callovian groundwater complex and an increase in mineralization in Bajocian aquifer (Kuraieva et al. 2020).

4 Material and methods

In this work, we took systematic, mathematical-statistical, and geo-informational approaches to the study of the object. Microsoft Excel, Statistica, and Attestat software packages were chosen for mathematical and statistical processing; MapInfo Professional 6.5 and ArcGIS-ArcMap 9.3 programs were used to construct cartographic schemes. To study the chemical composition of artesian well-room water, generally accepted physicochemical and chemical methods of analysis were used: general chemical analysis; titration; atomic emission spectral analysis, atomic potentiometric method. and absorption analysis. Microelement analysis of water samples was performed using the method of mass spectrometry with inductively coupled plasma (ICP-MS) on a mass spectrometer with dual focusing of the ion beam ELEMENT-2 by Thermo Scientific (Thermo Electron GmbH, Bremen), which operates based on M.P. Semenenko Institute of geochemistry, mineralogy and ore formation of the National Academy of Sciences of Ukraine. To obtain signal-concentration calibrations, a certified standard (ICP multielement standard solution VI, by Merck KGaA) was used, from which a series of 6 calibration standards from 1 to 1000 ppb was made. Samples and standards preparations were performed by weight. Purified water using Millipore-O3 (Millipore SA, France) was used to prepare the solutions. The method of thermodynamic modeling using the GEMS software was used to determine the migration forms of microelements in groundwater.

5 Results and discussion

5.1 Macrocomponent composition features

During 2007–2012, a monitoring study of the chemical composition of underground water in Kyiv was conducted by Zlobina (2013). In the course of these studies, samples from 163 well-rooms, exploiting the Cenomanian-Callovian groundwater complex and Bajocian aquifer were taken. This enabled us to construct cartographic schemes of elements content in groundwater and to assess their spatial distribution for the studied area. Examples of such cartographic schemes for Ca, Mg, and Cl in the Cenomanian-Callovian groundwater complex are presented in Figs. 2, 3 and 4.

To determine the patterns of changes in the chemical composition of the studied groundwater complex within the city of Kyiv in connection with technogenic influence, changes in the main components over time were studied. Library materials with the results of macrocomponent analysis of water samples from the Cenomanian-Callovian groundwater complex were analyzed by Koshliakova (2015). The selection covers data from the 1980s to the 2010s (a total of 298 wells, both well-room, and production). Such indicators of chemical composition as mineralization, oxidizability, hardness, pH, and the content of

Ca, Mg, Na + K, Fe, Cl, and SO₄ ions were considered. The study of the ratio between changes in indicators and the amount of water intake was carried out for the observation period time from 1980 to 2010. This period is marked by a decrease in the volume of water intake. Considering the intensity of water intake as one of the key factors of man-made influence on the hydrogeological system of the Cenomanian-Callovian groundwater complex (which determines the hydrodynamic conditions of the depression funnel formation), the indicators of the chemical composition were normalized by its amount.

The calculation of normalization was executed according to the following formula:

$$C_{(Q)} = C/Q$$

where $C_{(Q)}$ is the normalized indicator of the chemical composition of water, *C* is the concentration of the indicator of the chemical composition of water, mg/L, *Q* is the amount of water intake, thousand m³/day.

A graphic representation of the relationship between changes in the normalized indicators of the chemical composition of groundwater (for Ca, Mg, and Cl as an example) of the Cenomanian-Callovian groundwater complex and water intake intensity is provided in Figs. 2, 3 and 4.

The normalized value of mineralization increased with a decrease in water intake during 1980–2010, which indicates a relative increase in the content of mineral substances during long-term exploitation. A high negative correlation ($K_{cor.} = -0.54$ to -0.86) is also typical for normalized values of oxidizability, total hardness, pH, Ca, Mg, and Cl content (Table 1).

The achieved results demonstrate the sustainable environmental impact of changes in the hydrodynamic and hydrogeochemical conditions of active water exchange zone aquifers inherited during maximum water intake.

During 2019–2021, the authors conducted an additional survey of individual well-rooms in Kyiv to determine the dynamics of groundwater macrocomponent composition. The water samples' chemical composition was graphically submitted in form of Durov plots. Figure 5 shows the example of a such plot for two representative well-rooms, No. 15 on the left bank of the Dnieper River (212 m in depth, Cenomanian-Callovian groundwater complex), and well No. 76, located on the right bank of the Dnieper River (95 m in depth, Bajocian aquifer).

Comparative analysis of the diagrams revealed that the macrocomponent composition of the deeper, Bajocian aquifer, remains stable, once for the Cenomanian-Callovian groundwater complex, there is a tendency to decrease hydrogen carbonates and increase chlorides and sulfates, whereas the cation composition remains relatively stable.



Fig. 2 Ca content in Cenomanian-Callovian groundwater complex within Kyiv. a map-scheme of Ca distribution as of 2007–2012; b the dynamics of changes in normalized indicators of Ca and water intake in the period 1980–2010



Fig. 3 Mg content in Cenomanian-Callovian groundwater complex within Kyiv. a map-scheme of Mg distribution as of 2007–2012; b the dynamics of changes in normalized indicators of Mg and water intake in the period 1980–2010



Fig. 4 Cl content in Cenomanian-Callovian groundwater complex within Kyiv. a map-scheme of Cl distribution as of 2007–2012; b the dynamics of changes in normalized indicators of Cl and water intake in the period 1980–2010

 Table 1
 The results of the correlation analysis between indicators of groundwater chemical composition and water intake

Chemical composition indicator	Groundwater intake, thousand m ³ /day
Mineralization	- 0.84
Oxidizability	- 0.54
Total hardness	- 0.85
рН	- 0.86
Ca	- 0.72
Mg	- 0.75
Cl	- 0.6

Fig. 5 Durov plot depicting macrocomponent distribution for water samples taken from Kyiv's well-rooms. well No. 15. Cenomanian-Callovian groundwater complex, as of 2019 and 2021; well No.76. Bajocian aquifer, as of 2012 and 2021



Optionally, for these representative wells, such indicators as mineralization, total hardness, pH value, and iron content were analyzed. Respective diagrams were constructed (Fig. 6).

As a result of the analysis, the following patterns were revealed. During 2012–2023, mineralization in well No.15 increased significantly (by 55%), while in well No.76, this indicator remained relatively stable, with a tendency to decrease (by 21%). A general tendency towards a slight decrease in the value of the total hardness was revealed for both observation wells (during 11 years this indicator decreased by 6% in well No.15, and by 13% in well No.76). The pH value remained stable during the observation period for both wells, the changes are insignificant (in well No.15 this indicator increased by 3%, in well No.76, decreased by 6%). Significant changes are observed in iron concentration (during 11 years of exploitation, the iron content in well No.15 increased by 5.5 times, and in well No.76, decreased by 5 times). The authors believe that such significant changes in iron concentration can be related to the equipment condition of the water intake facilities themselves. Since the studied wells have been operated for a long time, during which no replacement of the casing pipes was carried out, it is quite likely that their technical condition is unsatisfactory and corrosion of the metal from which the equipment of the pump stations is made has occurred. Therefore, the results of the chemical analysis of water samples for iron content obtained in the laboratory are not relevant. Despite this, the obtained results are consistent with previous conclusions (the groundwaters of the Bajocian aquifer are more stable in terms of their chemical composition than the waters of the Cenomanian-Callovian groundwater complex).

Such differences in the two studied aquifers can be explained as follows. As indicated in the work (Koliabina et al. 2021), the processes of direct ion exchange and precipitation/dissolution of minerals, as well as the processes of reverse ion exchange and precipitation/dissolution of minerals, play a significant role in the formation of the water composition of Bajocian aquifer; and the role of processes of ion exchange and precipitation/dissolution of minerals increases with an increase in calcium



Fig. 6 Diagram of changes in indicators of the groundwater's chemical composition during 2012–2023. **a** mineralization (mg/L), **b** total hardness (mmol/L), **c** pH value, **d** iron content (mg/L)

concentration and a decrease in sodium concentration in water. The process of chemical composition formation of the Cenomanian-Callovian groundwater complex is characterized by its peculiarities: first, waters balanced by sodium and chlorine enter the aquifer, then, as a result of ion exchange and as a result of the precipitation of montmorillonite and illite, sodium is removed from the waters. Minor variations of this element are caused by the buffering properties of minerals of the montmorillonite group, which are settled in aquifer conditions. An important role is also played by regionally spread weakly permeable layers: the stratum lying above the Cenomanian-Callovian groundwater complex, confining bedrocks of the chalk and marl strata of the Upper Chalk, $K_2km + k$ (average thickness within Kyiv varies between 60 and 130 m), and the layer, which separates the studied aquifers, confining bedrocks of Pidluzhna, Nizhynska, and Ichnianska formations, $J_2pd + i\check{c}$ (average thickness 86 m).

According to Yakovlev (2011), in the formation of the depression funnel, the diffusion-convective motion of salts and microcomponents from the weakly permeable (separating) layer is a significant factor in influencing the hydrogeochemical composition of the waters of operational

aquifers. Regional low-permeability layers contain large volumes of groundwater and dissolved salts of many chemical elements. During operational pressure relief in permeable layers, de-compaction of adjacent weakly permeable layers occurs, and slow migration of mineralized pore solutions develops. The longtime development of depression funnels and their large areas in operational aquifers determine the significant influence of low-permeability layers on the formation of ecological-hydrogeological conditions of underground withdrawals. Under conditions of operational decrease in pore water pressure, there is an increase in the equilibrium pressure of the mineral skeleton, part of the compression deformation of which is transferred to a weakly permeable (separating) layer in the form of initial decompaction and subsequent partial compression (Bolton-Jackson effect). The impact of the aforementioned changes in the stress state of the hydrogeofiltration system reaches 1–2% of its total volume. However, during long-term operation of water withdrawal (10-20 years and more), a stable diffuse-convective transfer of porous solutions salts from confining layer is formed, the mineralization of which up to 1-2 orders of magnitude can exceed the mineralization of operational

aquifers water. According to the existing hydrogeofiltration model, the separating layers have a double structure of pore space due to the existence of weakened linear zones of high permeability and stable weakly permeable blocks. Therefore, in the case of vertical water exchange, boundary sections of the above zones acquire stable flow rates and slow molecular diffusion. At the same time, the contact zones of weakly permeable areas, as long as they are compressively de-compacted and the depression funnel gradually develops, are a practically stable source of highly mineralized pore solutions flow.

Therefore, the presence of a stable man-made factor (long-term water exploitation with the formation of depression funnels), and the weak protection of the Cenomanian-Callovian groundwater complex in comparison with the Bajocian aquifer, determine the differences in the dynamics of changes in the chemical composition of the studied interlayer waters over time.

5.2 Microcomponent composition features

During 2007–2012, Zlobina (2013) conducted monitoring studies on the content of microelements in well-room water in Kyiv. Also, archival data on trace element composition for 1999–2002 were analyzed. Statistical processing

proceeded. The results are graphically presented in the form of diagrams (Fig. 7).

The following regularities were found (Zlobina 2013):

Microelements distribution in Cenomanian-Callovian groundwater complex:

Fe From 1999 to 2002, the maximum metal content was 2.5 mg/L, which is 12.5 times higher than the MPC according to Ukrainian regulatory documents, from 2006 to 2012, it was 0.73 mg/L, which is 3.7 times higher exceeds the MPC, but its average content remains unchanged as 0.19 mg/L (at MPC 0.2).

Mn From 1999 to 2002, the maximum content of the element was 0.4 mg/L, which is 8 times higher than the MPC, from 2006 to 2012; -0.25 mg/L was recorded, which is 5 times higher than the MPC, however, its average content remains unchanged -0.03 mg/L (at the MPC of 0.05 mg/L).

Cu Maximum concentration of the element was 0.018 mg/L (1999–2002) and 0.075 mg/L (2006–2012). The copper content in no case exceeded the MPC (1.0 mg/L) and did not differ on average: 0.001-0.002 mg/L.

Sr Maximum concentration of the element was 1.7 mg/ L (1999–2002); 0.85 mg/L (2006–2012). Its content did not exceed the MPC (7.0 mg/L), on average 0.53–0.38 mg/L.



Fig. 7 Diagram of microelements content in potable interlayer water: **a** and **b** 1999–2002; **c** and **d** 2006–2012. *Notes* filled triangle: minimum content, asterisk: maximum content, open circle: mean content (median), filled square: maximum permissible concentration (MPC)

F From 1999 to 2002, the maximum content of the element was 0.67 mg/L, from 2006 to 2012, 0.61 mg/L. The concentration did not exceed the MPC (1.5 mg/L), remaining unchanged on average 0.3 mg/L.

Cr The maximum metal content was determined, from 1999 to 2002, 0.003 mg/L, from 2006 to 2012, 0.01 mg/L. There was no case of exceeding the MPC of the element (0.05 mg/L); its average content was 0.0008 mg/L (1999–2002), 0.002 mg/L (2006–2012).

Microelements distribution in Bajocian aquifer:

Fe From 1999 to 2002, the maximum metal content was, 1.56 mg/L, which is 7.8 times higher than the MPC, from 2006 to 2012, it was 1.62 mg/L, which is 8.1 times higher than the MPC, but its average content remains unchanged at 0.24 mg/L.

Mn From 1999 to 2002, the maximum content of the element was 0.35 mg/L, which is 7 times higher than the MPC, from 2006 to 2012, 0.65 mg/L was recorded, which is 13 times higher than the MPC at the established average content: in 1999–2002, 0.018 mg/L, in 2006–2012, 0.03 mg/L.

Cu During the entire period of research, its maximum content remained almost unchanged as 0.009 mg/L, the concentration did not exceed the MPC and was, on average, from 0.001 mg/L (1999–2002) to 0.002 mg/L (2006–2012).

Sr From 1999 to 2002, the maximum metal content was 1.5 mg/L, and from 2006 to 2012, 1.1 mg/L. Its content did not exceed the MPC, being on average 0.8–0.45 mg/L.

F From 1999 to 2002, the maximum concentration of the element was 1.1 mg/L, with an average content of 0.65 mg/L. From 2006 to 2012, the maximum content was 1.0 mg/L, with an average of 0.5 mg/L. Its concentration in no case exceeded the MPC. The maximum and average content of fluorine in the Bajocian aquifer is 1.5 times higher than in the Cenomanian-Callovian groundwater complex, which could be taken into account in the case of mixed source pumping wells.

Cr From 1999 to 2002, the maximum metal content reached: 0.004 mg/L, from 2006 to 2012, 0.02 mg/L. There was no case of exceeding its MPC, its average content was: 0.0008 mg/L (1999–2002), 0.003 mg/L (2006–2012).

Considering the relevance of the problem of groundwater pollution by heavy metals, in 2019, the authors additionally conducted a study of the content of Pb, Mo, Cu, and Zn within the boundaries of the Kyiv underground water deposit (Kuraieva et al. 2020). By use of statistical methods, the results of chemical analysis of water for 123 well-rooms were processed, among which 68 operate the Cenomanian-Callovian groundwater complex, and 55 in the Bajocian aquifer. The graphic representation of some Acta Geochimica (2023) 42:535-551

heavy metals' distribution is executed in the form of histograms (Fig. 8).

On average, the concentration of heavy metals in the Bajocian aquifer is higher than in the overlying Cenomanian-Callovian groundwater complex. It is most likely can be connected with a natural factor, in the water-bearing rocks of the Bajocian aquifer, there are lenses of brown coal (black lignite), which can potentially contain impurities of heavy metals in its composition. Also, according to the authors, lead can come as a result of upward filtration from the aquifer in the deposits of Dronivska and Serebryanska formations of the Lower Triassic, which lies at a depth of 300–350 m and is characterized by varied chemical composition.

Exceeding the MPC for the lead was found in three wellrooms under investigation. These are wells numbered 2, 94, and 15, located on the right bank of the Dnieper River, in its floodplain. According to the map of soil contamination of Kyiv with heavy metals, these wells are located in areas of the city with a slight and medium level of total pollution, in particular lead. It is worth noting that all three wellrooms are geomorphologically located in the Dnieper River valley, which belongs to the zone of distribution of groundwater, conditionally protected from contamination from the surface. This is because two powerful confining bed layers are wedged in this zone in the geological crosssection, a layer of variegated and red-brown clays of the Miocene-Pliocene and a layer of marls of the Kyivska and Obukhivska formations of the Eocene, as well as aquifers of Quaternary, alluvial-diluvial deposits, alluvial deposits of the middle Neopleistocene and Oligocene-Miocene sediments. In addition, large local depression funnels of the Cenomanian-Callovian groundwater complex can be observed along the Dnieper River valley.

5.3 Ecological and geochemical aspects

An important indicator of the biogeochemical quality of potable groundwater is seen less as the presence of high gross content of a chemical element, and more as the form of its migration. Migration form determines the features of geochemical transfer in the components of the environment, the biological significance of the component for a living organism, the speed of its transit through the trophic chain, accumulation, and toxicity (Zlobina 2013).

In terms of ecology and human health, the biogeochemical effect of complex states of elements is not relevant to the effect of their simple forms. In its simplest form, this means that the degree of its influence on the body depends on the form of migration of the element. For example, cationic forms of copper $[Cu^{2+}, CuOH^+, Cu_2(-OH)_2^{2+}]$ are much more harmful than their neutral or anionic forms. At the same time, the toxicity of





Fig. 8 Heavy metals distribution in Kyiv well-rooms (as of 2019)

organometallic forms of Pb and Hg is sometimes orders of magnitude stronger than that of inorganic forms. The binding of heavy metals, Cd, Cu, Pb, Hg, in fulvate and humic complexes significantly reduces their harmful effects.

For physico-chemical modeling of trace elements, the authors used the GEMS software complex based on the Gibbs energy minimization method. This program is an improved and expanded version of the Selector-S program, developed under the leadership of I.K. Karpov. It was significantly modified by the creative team under the guidance of D.O. Kulik in cooperation with the team of I.K. Karpov, first at the Metallogeny Department of the Institute of Geochemistry and Geophysics of Minerals of the National Academy of Sciences of Ukraine and State Enterprise "Technocenter" (Ukraine), and then at the Paul Scherer Institute (Switzerland).

To model the migration of microelements using the GEMS software complex, the averaged chemical composition determined by spectral semi-quantitative analysis and the ICP-MS method, obtained based on the 2007–2012 selection (number of samples: 84 for Cenomanian-Callovian groundwater complex, 34 for Bajocian aquifer). The simulation results are shown in Table 2. The simulation result shows that both aquifers are characterized by the predominant migration of the following metals in the cationic form (aqua-ions): Ca, Mg, Na, Ba, Co, Cu, Mn, Ni, Sr, Zn. The difference between the calculated and experimentally determined pH does not exceed 8% for the Bajocian aquifer and 5% for the Cenomanian-Callovian groundwater complex (Zlobina 2013).

Thus, it was established that the main forms of metal migration in the Cenomanian-Callovian groundwater complex and Bajocian aquifer are free uncomplexed ions, carbonate, and hydroxo complexes. In the Bajocian aquifer, the migration of metals in the form of simple sulfate and chloride complexes is observed, which is explained by some increase in the content of chlorides and sulfates, and by the change in redox conditions.

The assessment of the microelement composition of Kyiv's potable groundwater made it possible to determine the number of trace elements that are interesting in terms of their impact on the population's health. For the ecologicalgeochemical assessment of the quality of Kyiv groundwater, used for potable supply, the criterion of biologically significant concentrations (BSC) was applied.

In the work (Barvish and Shvarts 2000) for the waterhuman ecological system from a medical and biological

Element migration form Percentage Element migration form Percentage Ag^+ 89.7% Ag^+ 35.27% $AgCl^-$ 0.07% $AgCl^-$ 9.15% $AgCl^-$ 10.09% $AgCl^-$ 9.15% $AgCl^-$ H_AOQ^- 21.60% $BaQCO_1^0$ 0.000% $HaO_1^-2^-$ 78.40% $Ba(CO_1)^0$ 0.17% Ba(CO_1)^0 0.15% $Ba(SO1)^0^-$ 0.34% Ba(CO_1)^0^- 13.55% $Ba(SO1)^0^+$ 0.34% Ba(SO1)^0^- 13.58% Ba^{-2}^- 95.08% Ba^{-2}^- 0.65% BeC^0^- 7.36% $BeOH^+$ 0.65% $BeC0^+$ 0.38% $Ba(CO_1)^0^-$ 0.35% $Ba(CO_1)^0^+$ 0.38% $BeOH^+$ 0.65% $BeC0^+$ 0.66% $Ca(CO3)^0^-$ 0.75% $Ca(CO3)^0^-$ 0.92% Ca(CO3)^0^- 0.75% $Ca(CO3)^0^-$ 0.92% Ca(CO3)^0^- 0.84% $Ca(CO3)^0^-$ 0.23%	Cenomanian-Callovian groundwater	complex	Bajocian aquifer			
A_r^+ 89.7% Ag^+ 35.27% $AgCl_r^-$ 0.07% $AgCl_r^-$ 9.15% $AgCl_r^-$ 10.09% $AgCl_r^-$ 21.69% $IIAo_r^-$ II_AO_r^-^- 21.69% $IIAo_r^-$ 100.09% $IIao_r^-^-$ 78.40% $Ba(Co_r)^0$ 0.17% $Ba(Co_r)^0^-$ 0.13% $Ba(HCO_r)^+$ 4.44% $Ba(HCO_r)^+$ 3.63% $Ba(YOP)^0$ 0.39% $Ba(SOP)^0$ 1.39% $Ba(YCO_r)^+$ 0.30% $Ba(SOP)^0$ 1.39% $Ba(YCO_r)^+$ 0.30% $Ba(YCO_r)^+$ 3.63% $Ba(YCO_r)^+$ 0.39% $Ba(YCO_r)^+$ 1.39% $Ba(YCO_r)^+$ 0.39% $Ba(YCO_r)^+$ 3.63% $Ba(YCO_r)^+$ 9.13% $Ba(YCO_r)^+$ 9.24% $Ba(YCO_r)^+$ 9.13% $Ba(YCO_r)^+$ 9.24% $Ba(YCO_r)^+$ 9.13% $Ba(YCO_r)^+$ 9.25% $Ba(YCO_r)^+$ 9.25% $Ba(YCO_r)^+$ 9.25% $Ba(YCO_r)^+$ 9.25% $Ba(YCO_r)^+$ 0.75% $Ca(YCO_r)^+$ 9.25%	Element migration form	Percentage	Element migration form	Percentage		
AcC1-0.07%AcC1-9.15%AgC1010.09%AgC255.47%HANO,HANO,-10.08%BIACO,0100.00%MasO,-278.40%BIACO,00.17%BIACO,0 ¹ 3.63%BIACO,0 ¹ 0.39%BIACO,1 ¹ 3.63%BIACO,1 ¹ 0.39%BIACO,1 ¹ 9.66%BIACO,1 ¹ 0.48%BIACO,1 ¹ 9.26%BIACO,1 ¹ 0.39%CalCO,1 ¹ 8.23%CalCO,1 ¹ 0.92%CalCO,1 ¹ 8.23%CalCO,1 ² 0.92%CalCO,1 ¹ 8.23%CalCO,1 ² 0.92%CalCO,1 ¹ 8.23%CalCO,1 ² 0.92%CalCO,1 ¹ 8.23%CalCO,1 ² 0.01%CalCO,1 ¹ 8.23%CalCO,1 ¹ 0.01%CalCO,1 ¹ 8.23%CalCO,1 ¹ 0.01%CalCO,1 ¹ 0.14%CalCO,1 ¹ 0.01%CalCO,1	Ag^+	89.7%	Ag^+	35.27%		
AqC1 ⁶ 10.09%AqC7 ⁶ 55.47%HyAQ7 ⁻¹ -HyAQ7 ⁻¹ 21.00%HAQ2100.00%HaQ7 ⁻² 78.40%Ba(CQ0) ⁰ 0.17%Ba(CQ0) ⁰ 0.13%Ba(CQ0) ¹ 4.44%Ba(ICQ) ^{1/2} 3.63%Ba(CM1 ⁰)0.30%Ba(SOU1 ⁰)3.63%Ba ⁺² 0.55%Ba ⁺² 0.65%Ba ⁺² 0.55%Ba ⁺² 0.65%Bc ⁰ 7.36%Bc ⁰ 0.55%Bc ¹ 0.48%BiO ¹ 0.55%Bo ¹ 0.48%BiO ¹ 0.55%Bo ¹ 0.48%BiO ¹ 0.55%Bo ¹ 0.92%Ca(CQ0) ¹ 0.55%Ca(CQ3) ⁰ 0.92%Ca(CQ0) ¹ 8.23%Ca(CQ0) ¹ 0.54%Ca(CQ0) ¹ 8.23%Ca(CQ0) ¹ 0.92%Ca(CQ0) ¹ 8.23%Ca(CQ0) ¹ 0.92%Ca(CQ0) ¹ 8.23%Ca(CT ¹ 0.00%Ca(T ¹ 0.05%Ca ¹ ² 9.17%Ca ¹ ² 9.10%Ca(T ¹ 0.01%Ca ¹ ² 9.10%Ca(T ¹ 0.13%Ca(CT ¹ 0.15%Ca(C1) ¹ 0.13%Ca(C1) ^{1/2} 0.22%Ca ¹ ² 9.80%Ca ¹ ² 9.10%Ca(T ¹ 0.15%Ca ¹ ² 9.49%Ca ¹ ² 9.80%Ca ¹ ² <td>$AgCl_2^-$</td> <td>0.07%</td> <td>$AgCl_2^-$</td> <td>9.15%</td>	$AgCl_2^-$	0.07%	$AgCl_2^-$	9.15%		
H _A AO ₄ -H _A AO ₄ 21.60%HAAO21000%HaAO7278.40%BA(CO) ⁰ 0.17%Ba(CO) ¹ 0.35%Ba(CO) ¹ 0.30%Ba(CO) ¹ 35.35%Ba(CO) ¹ 0.30%Ba(CO) ¹ 35.36%Ba ⁺² 0.50%Ba ⁺² 0.55%Ba ⁺² 0.59%Ba ⁺² 0.55%Bc ⁰ 7.36%Bc ⁰¹ 20.66%BcO ¹ 9.98%BcO ¹ 20.66%BCO ¹ 9.92%Ca(CO3) ⁰ 0.72%Ca(CO3) ⁰ 0.22%Ca(CO3) ⁰ 0.72%Ca(CO3) ⁰ 0.22%Ca(CO3) ⁰ 0.78%Ca ⁺² 89.17%Ca(F ⁺² 80.15%Ca ⁺² 0.01%Ca ⁺² 80.5%Ca ⁺¹ 0.00%Ca ⁺² 80.5%Ca ⁺¹ 0.01%Ca ⁺² 80.5%Ca ⁺¹ 0.01%Ca ⁺² 91.0%Ca ⁺¹ 0.13%Ca(O1 ⁺¹ 0.1%Ca ⁺¹ 0.13%Ca ⁺¹ 0.1%Ca ⁺¹ 0.13%Ca ⁺¹ 0.2%Ca ⁺¹ 0.16%Ca ⁺¹ 0.2%Ca ⁺¹ 0.16%Ca ⁺¹ 0.2%Ca ⁺¹ 0.00%Ca ⁺¹ 0.2%Ca ⁺¹ 0.00%Ca ⁺¹ 0.1%Ca ⁺¹ 0.00%Ca ⁺¹ 0.2%Ca ⁺¹ 0.00%Ca	$AgCl^0$	10.09%	$AgCl^0$	55.47%		
HadO21000%HadO2Ra(CO1)00.13%Ba(CO1)00.17%Ba(CO1)00.13%Ba(CO1)00.30%Ba(CO1)013.98%Ba(CO1)10.30%Ba(CO1)113.98%Ba ⁺² 0.50%Ba ⁺² 0.55%Bc ⁰ 0.50%Be ⁺² 0.55%Bc ⁰ 0.48%BiO ⁺¹ 92.66%BiO ⁺¹ 0.48%BiO ⁺¹ 92.66%BiO ⁺¹ 0.48%BiO ⁺¹ 9.53%Ba(CO1) ¹ 9.52%BiO ₂ H ² 9.74%Ca(CO3) ⁰ 0.23%Ca(CO1) ¹ 8.23%Ca(CO1) ¹ 9.68%Ca(HCO1) ¹ 8.23%Ca(CO1) ² 0.23%Ca(CO1) ² 80.15%Ca ⁺² 9.17%Ca(C1 ⁺¹ 0.05%Ca ⁺² 0.01%Ca ⁺² 91.10%Ca ⁺² 0.01%Ca ⁺² 91.10%Ca ⁺² 0.13%Ca(T ⁺¹ 0.05%Ca ⁺¹ 0.13%Ca(H ⁺¹ 0.11%Ca(C0) ¹⁺ 9.43%Ca(C1 ⁺¹ 0.15%Ca ⁺¹ 0.13%Ca(H ⁺¹ 0.15%Ca(C ⁺¹ 0.13%Ca(H ⁺¹ 0.15%Ca(C ⁺¹ 0.15%Ca ⁺² 9.9.0%Ca ⁺¹ 0.15%Ca ⁺¹ 0.16%Ca ⁺¹ 0.15%Ca ⁺¹ 0.16%Ca ⁺¹ 0.15%Ca ⁺¹ 0.16%Ca ⁺¹ 0.15% <t< td=""><td>$H_2AsO_4^-$</td><td>_</td><td>$H_2AsO_4^-$</td><td>21.60%</td></t<>	$H_2AsO_4^-$	_	$H_2AsO_4^-$	21.60%		
Ba(CO) ⁹ 0.17%Ba(CO) ⁹ 0.13%Ba(ILCO) ¹⁺ 4.44%Ba(ILCO) ¹⁺ 3.63%Ba(SOL) ⁰ 0.30%Ba(SOL) ⁰ 1.39%Ra ^{1,2} 95.08%Ra ^{1,2} 82.24%Bc ⁰¹ 7.36%Bc ⁰² 0.65%Bc ⁰¹ 7.36%Bc ⁰¹ 0.65%Bc ⁰¹ 9.98%Bc ⁰¹ 0.53%BiO, ¹¹ 9.98%BiO, ¹¹ 9.26%BiO, ¹¹ 9.98%Ca(CO3) ⁹ 0.24%Ca(CO3) ⁰ 0.23%Ca(CO3) ⁰ 0.184%Ca ¹² 9.17%Ca(CO1) ¹⁺ 0.15%Ca ¹² 9.17%Ca(C1 ¹⁺ 0.01%Ca ¹² 9.17%Ca(C1 ¹⁺ 0.01%Ca ¹² 9.13%Ca ¹² 9.10%Ca ¹² 9.43%Ca ¹² 9.10%Ca ¹² 0.01%Ca ¹² 9.10%Ca ¹² 9.43%Ca ¹² 9.10%Ca ¹² 0.13%Ca ¹² 9.10%Ca ¹² 0.13%Ca ¹² 9.10%Ca ¹² 0.15%Ca ¹² 0.22%Ca ¹² 0.15%Ca ¹² 0.22%Ca ¹² 0.15%Ca ¹² 0.22%Ca ¹² 0.16%Ca ¹² 0.21%Ca ¹² 0.16% <t< td=""><td>HAsO₂</td><td>100.00%</td><td>$HasO_4^{-2}$</td><td>78.40%</td></t<>	HAsO ₂	100.00%	$HasO_4^{-2}$	78.40%		
Ba(IICO,)*4.44%Ba(IICO,)*3.63%Ba(SO1)*0.30%Ba(SO1)*13.98%Ba(*2)0.50%Ba(*2)8.24%Be*20.59%Be*20.65%BcO1*0.98%BcO1*9.26%BiO10.48%BiO1*0.53%BiO1*0.48%BiO1*0.53%BiO1*0.48%BiO1*0.53%BiO1*0.48%BiO1*0.53%BiO1*0.48%BiO1*0.53%Ca(CO3)*0.22%Ca(CO3)*0.72%Ca(CO3)*0.23%Ca(CO3)*0.18%Ca(CO1)*0.05%Ca(T1*0.05%Ca(T2*0.01%CaT2*0.15%Ca(T2*0.01%CaT2*0.15%Ca(T2*0.13%Ca(T1*0.01%Ca(T2*0.13%Ca(T1*0.11%Ca(T2*0.13%Ca(T2*9.10%Ca(T2*0.13%Ca(T2*9.10%Ca(T2*0.53%Ca(T2*9.49%Ca(T2*0.53%Ca(T2*9.49%Ca(T2*0.17%Ca(T2*9.49%Ca(T2*0.17%Ca(T2*9.49%Ca(T2*0.16%Ca(T2*9.49%Ca(T2*0.16%Ca(T2*9.49%Ca(T2*0.16%Ca(T2*9.49%Ca(T2*0.16%Ca(T2*9.49%Ca(T2*0.16%Ca(T2*9.49%Ca(T2*0.06%HerOa*1.53%Ca(T2*0.06%Ca(T2*9.41%Ca(T2*0	$Ba(CO_3)^0$	0.17%	$Ba(CO_3)^0$	0.13%		
Ba(SO4)°0.30%Ba(SO4)°13.9% Ba^{+2} 95.08% Ba^{+2} 0.65% Bc^{+2} 0.59% Ba^{+2} 0.65% Bc^0 7.36% $Bc0^0$ 6.64% $BcO1^+$ 91.98% $Bc01^+$ 0.53% BiO^+ 0.48% BiO^+ 0.53% BiO_2H^0 99.52% BiO_2H^0 99.47% $Ca(CO3)^0$ 0.22% $Ca(CO3)^0$ 0.72% $Ca(SO_4)^0$ 0.23% $Ca(SO_4)^0$ 10.84% Cat^{+2} 89.17% Ca^{+2} 80.15% Cat^{+2} 0.00% Cat^+ 0.01% Cat^{+2} 0.01% Cat^+ 0.01% $Catt^+$ 0.01% Cat^+ 0.01% $Catt^+$ 0.01% Cat^+ 0.01% $Catt^+$ 0.01% Cat^+ 0.02% $Catt^+$ 0.01% Cat^+ 0.02% $Catt^+$ 0.02% Cat^+ 0.02% $Catt^+$ 0.02% Cat^+ 0.02% $Catt^+$ 0.02% Cat^+ 0.02% $Catt^+$ 0.02% Cat^+ 0.03% $Catt^+$	$Ba(HCO_3)^+$	4.44%	$Ba(HCO_3)^+$	3.63%		
Bat ⁻² 95.08%Bat ⁻² 82.24%Be ⁺² 0.59%Be ⁻² 0.65%BeO ⁰ 7.36%BeO ⁰ 0.65%BrOth9.198%BrOth92.66%BrOth0.48%BrOth0.53%BrOth0.92%Ca(CO3) ⁰ 0.72%Ca(CO3) ¹ 0.92%Ca(CO3) ⁰ 0.72%Ca(CO3) ¹ 0.92%Ca(CO3) ⁰ 0.72%Ca(CO3) ¹ 0.92%Ca(CO3) ⁰ 0.72%Ca(SO4) ¹ 0.88%Ca(CO3) ⁰ 0.72%Ca(SO4) ¹ 0.05%Ca(C1) ¹ 0.84%Ca ¹² 89.17%Ca ¹² 0.53%Ca ¹⁷ 0.01%Ca ¹² 0.55%Ca ¹⁷ 0.01%Ca ¹² 0.5%Ca ¹⁷ 0.01%Ca ¹² 0.5%Ca ¹⁷ 0.13%Ca(C1 + Co1) ¹⁺ 0.11%Ca(C3) ¹⁺² 0.33%Ca(C1 + Co1) ¹⁺² 0.11%Ca(C3) ¹⁺² 0.13%Ca(H1 + 0.11%0.11%Ca(C4) ¹⁺² 0.13%Ca(C1 + 0.22%0.22%Ca ¹² 0.13%Ca(H1 + 0.15%0.22%Ca ¹⁴ 0.17%Ca ¹² 0.22%Ca ¹⁴ 0.28%CaC1 + 0.35%0.22%Ca ¹⁴ 0.28%CaC1 + 0.35%0.21%CaO ¹⁴ 0.16%CaCH + 0.15%0.53%CaO ¹⁴	Ba(SO4) ⁰	0.30%	$Ba(SO4)^0$	13.98%		
Bet ² 0.59%Bet ² 0.65%BC07.36%Be06.64%BC0H*9.26%Be0H*9.26%BiO+0.48%BiO+0.53%BiO,H ⁰ 9.92%BiO,H ⁰ 9.47%Ca(CO3) ⁰ 0.92%Ca(CO3) ⁰ 0.72%Ca(HCO,) ⁺ 9.88%Ca(HCO,) ⁺ 8.33%Ca(SO,0) ⁰ 0.23%Ca(CO3) ⁰ 10.84%Ca ⁺² 89.17%Ca ⁺² 80.15%CaC ⁺¹ 0.00%CaC ⁺¹ 0.01%CaC ⁺¹ 0.11%CaC ⁺¹ 0.01%CaC ⁺¹ 0.11%CaC ⁺¹ 0.13%CaOH+0.11%Ca(CO,1) ⁺¹ 9.43%CaC(O) ⁺¹ 0.16%CaOH+0.13%Ca(CO) ⁺² 0.22%Ca ⁺² 0.98%Ca ⁺² 0.29%CaC ⁺¹² 0.29%CaC ⁺¹² 0.29%CaC ⁺¹² 0.17%CaH ⁻¹² 0.25%CoOH+0.16%CaOH+0.15%CoOH+0.16%CaOH+0.15%CaO ⁺¹² 0.99%CaC ⁺² 0.29%CaC ⁺¹² 0.09%CaC ⁺¹² 0.29%CaC ⁺¹² 0.00%CaC ⁺¹² 0.29%CaC ⁺¹⁴ 0.00%CaC ⁺² 0.15%CaO ⁺¹⁴ 0.16%CaOH+0.15%CaO ⁺¹⁴ 0.16%CaO ⁺¹⁴ 0.15%CaO ⁺¹⁴	Ba^{+2}	95.08%	Ba^{+2}	82.24%		
Be0 ⁰ 7.36%Be0 ⁰ 6.64%Br0 ¹ 9.19%Br0H ¹ 9.26%Bi0 ¹ 0.48%Bi0 ¹ 0.33%Bi0 ₂ H ⁰ 9.95%Bi0 ₂ H ⁰ 9.94%CalCO3) ⁰ 0.92%CalCO3) ¹ 0.72%CalGO3) ¹ 0.23%CalCO3) ¹ 0.84%CalGO4) ¹ 0.23%CalSO4) ² 0.84%Cal ² 8.01.5%CalSO4) ² 0.84%Cal ² 8.01.7%CalC ¹ 0.05%Cal ² 0.01%Cal ²⁺² 9.10%Cal ²⁺¹ 0.13%CalCH ⁴⁺² 9.10%Cal ²⁺² 0.33%CalCH ²⁺² 0.23%Cal ²⁺² 0.33%CalCH ²⁺² 0.23%Cal ²⁺² 0.33%Cal ²⁺² 0.23%Cal ²⁺² 0.33%Cal ²⁺² 0.23%Cal ²⁺² 0.23%Cal ²⁺² 0.23%Cal ²⁺² 0.23%Cal ²⁺² 0.23%Cal ²⁺² 0.93%Cal ²⁺² 0.23%Cal ²⁺² 0.93%C	Be ⁺²	0.59%	Be ⁺²	0.65%		
BeOH ⁺ 91,98%BeOH ⁺ 92,66%BiO ⁺ 0.44%BiO ⁺ dP0,53%BiO ₂ H ⁰ 99,52%BiO ₂ H ⁰ 99,47%Ca(CO3) ⁰ 0.92%Ca(CO3) ⁰ 0.72%Ca(EO ₂) ⁺ 9,68%Ca(HO ₂) ⁺ 823%Ca(SO ₄) ⁰ 0.23%Ca(SO ₄) ⁰ 0.84%Ca ⁺² 89,17%Ca ⁺² 80,15%Ca ⁺² 0.00%CaCl ⁺¹ 0.05%Cal ⁺¹ 0.00%CaCl ⁺¹ 0.01%Cal ⁺¹ 0.01%CaCl ⁺¹ 0.01%Cal ⁺¹ 0.13%CdOl ⁺¹ 0.11%Cal ⁰ 0.53%CdI(CO ₃) ⁺¹ 9,10%Cal ¹⁰ 0.13%CdOl ⁺¹ 0.15%Cal ¹¹ 0.53%CdI(CO ₃) ⁺¹ 0.62%Cal ¹¹ 0.53%CdI(CO ₃) ⁺² 0.25%Cal ¹¹ 0.53%CdI(CO ₃) ⁺² 0.25%Cal ¹¹ 0.53%CdI(CO ₃) ⁺² 0.62%Cal ¹¹ 0.53%CdI(CO ₃) ⁺² 0.25%Cal ¹¹ 0.53%CdI(CO ₃) ⁺² 0.25%Cal ¹¹ 0.53%CdI(CO ₃) ⁺² 0.25%Cal ¹¹ 0.53%CdI(CO ₃) ⁺² 0.5%Cal ¹¹ 0.5%Cal ¹¹ 0.5%Cal ¹¹ 0.05%Cal ¹¹ 0.5%Cal ¹¹ 0.00%Cal ¹¹ 0.5%Cal ¹¹	BeO ⁰	7.36%	BeO^0	6.64%		
BiO*0.48%BiO*0.53%BO,H°9.92%BIO,H°9.47%Ca(CO3)°0.92%Ca(CO3)°0.72%Ca(BO,0)°0.23%Ca(BO,0)°8.23%Ca(SO,0)°0.23%Ca(SO,0)°10.84%Ca*28.917%CaC1+8.05%CaF+0.00%CaC1+0.05%CaF+0.01%CaF+0.01%CaF+0.01%CaC+8.15%CaO+0.13%CaO+0.11%CaO+0.13%CaO+0.11%CaO+0.13%CaO+0.11%Ca(CO_3)+9.76%Ca(CO_3)+9.710%Ca(F*30.53%Ca(CO_3)+9.710%Ca(F*30.53%Ca(CO_3)+9.23%CaC+0.17%CaF*20.62%Ca+29.80%CaC+29.43%CaO+0.17%CaF*20.22%Ca+29.80%CaC+29.43%CaO+0.05%CaC+29.44%CaO+0.05%CaC+29.44%CaO+0.05%CaO+10.55%CaO+0.06%HerO_41.50%CrO+100.00%Cs+99.3%CaO+100.00%Cs+9.93%CaO+100.00%Cs+9.93%CaO+100.00%Cs+9.93%CaO+100.00%Cs+9.93%CaO+100.00%Cs+9.93%CaO+100.00%Cs+9.93%CaO+100.00%Cs+9.93% <td< td=""><td>$BeOH^+$</td><td>91.98%</td><td>$BeOH^+$</td><td>92.66%</td></td<>	$BeOH^+$	91.98%	$BeOH^+$	92.66%		
BiO ₂ H ⁰ 99.52%BiO ₂ H ⁰ 99.47%Ca(CO3) ⁰ 0.92%Ca(CO3) ⁰ 0.72%Ca(HOO ₃) ⁺ 9.68%Ca(HOO ₃) ⁺ 8.23%Ca(SO4) ⁰ 0.23%Ca(SO4) ⁰ 10.44%Ca ⁺² 89.17%Ca ⁺² 80.15%Ca(I ⁺ 0.00%Ca(I ⁺ 0.01%Cal ⁺¹ 0.00%Ca(I ⁺ 0.01%Cal ⁺² 9.43%Ca(I ⁺ 0.01%Cd ⁺² 9.43%Ca(CI ⁺ 6.77%CdOH ⁺ 0.13%CdOH ⁺ 0.11%Ca(CO ₄) ⁺ 9.53%Ca(HOO ₃) ⁺² 0.62%Ca ⁺² 9.80%Ca ⁺² 9.94%Ca ⁺² 9.80%Ca ⁺² 9.94%Co ⁺¹ 0.16%Co ⁺² 9.94%Co ⁺¹ 0.16%Co ⁺² 9.94%Co ⁺¹ 0.16%Co ⁺¹ 0.35%Co ⁺¹ 0.02%Co ⁺² 9.94%Co ⁺¹ 0.16%Co ⁺² 9.94%Co ⁺¹ 0.16%Co ⁺² 9.94%Co ⁺¹ 0.02%Co ⁺² 9.94%Co ⁺¹ 0.02%Co ⁺² 9.94%Co ⁺¹ 0.06%Hco ₄ ⁻² 4.7%Co ⁺¹ 0.00%Ca ⁺¹ 0.35%Co ⁺¹ 1000%Ca ⁺¹ 9.93%Ca ¹⁰ -Ca ¹⁰ 1.5%Co ¹¹ 1000%Ca ⁺¹ 9.93%Ca ¹¹ 1000%Ca ⁺¹ 9.93%Ca ¹¹ 1000%Ca ⁺¹ 9.93%Ca ¹¹ 1000%Ca ⁺¹ 9.93%Ca ¹¹ 1000%<	BiO ⁺	0.48%	BiO^+	0.53%		
Ca(CO3) ⁰ 0.92%Ca(CO3) ⁰ 0.72%Ca(HCO3) ¹ 8.23%Ca(SO4) ⁰ 8.23%Ca(SO4) ⁰ 0.23%Ca(SO4) ⁰ 10.84%Ca ¹² 89.17%Ca ¹² 80.15%CaCl ⁺¹ 0.00%CaCl ⁺¹ 0.05%CaF ⁺ 0.01%CaF ⁺ 0.01%Cd ⁺² 9.43%Cd ⁺² 9.310%CdCl ⁺ 0.33%CdCl ⁺¹ 6.77%CdOH ⁺ 0.13%CdCl ⁺¹ 6.77%CdOH ⁺ 0.13%CdCl ⁺¹ 6.77%Cd(Da) ¹ 97.64%Cd(Ca) ¹ 9.710%Ce(HCO3) ¹ 97.64%Ce(Ca) ¹ 9.70%Ce(HCO3) ¹ 9.53%Ce(HCO3) ¹² 0.62%Ce ⁺³ 1.5%Ce ⁺³ 1.97%CeF ⁺² 0.17%CaCl ⁺¹ 0.35%CoCl ⁺¹ 0.28%Co ² 9.94%CoCl ⁺¹ 0.16%CoOH ⁺¹ 0.15%CrO ² 0.06%HerOa ⁻¹ 0.35%CrO ² 0.06%HerOa ⁻¹ 1.53%CrO ¹ 3.09%CrOH ⁻² -CrO ⁴ 100.00%Ca ⁺¹² 0.17%CuO ¹ 100.00%Ca ⁺¹² 0.07%Cu ¹² 0.06%HerOa ⁻¹ 0.17%CuO ¹ 0.00%CuO ¹² -CuO ¹ 0.00%CuO ¹² -CuO ¹ 0.00%Cu ¹² -CuO ¹ 0.00%Cu ¹² -CuO ¹ 0.00%Cu ¹² -CuO ¹ 100.00%Cu ¹² -CuO ¹ 2.	BiO_2H^0	99.52%	BiO_2H^0	99.47%		
Ca(HCO,)+9.68%Ca(HCO,)+8.23%Ca(SO,0)0.23%Ca(SO,0)10.84%Ca ¹² 89.17%Ca ⁺² 80.15%CaC+0.00%CaC1+0.05%CaF+0.01%CaF+0.01%CaC+99.43%CdC1-6.77%CdOH+0.13%CdCH+0.11%Ce(CO,1)+97.64%Ce(CO,1)+97.10%Ce(CO,1)+95.35%Ce(HCO,1)+20.62%Ce ⁺³ 1.58%Ce ⁺³ 1.97%Ce ⁺¹² 0.17%Ce ⁺¹² 9.949%CoC1+0.02%CoC1+0.35%CoOH+0.16%CoOH+0.15%CrO2-0.06%HcO_4-1.53%CrO2+0.00%CoC1+0.35%CoOH+0.00%CrO,H-CrO2+0.00%CrO,H-CrO2+0.00%CrO,H-CrO1+20.00%CrO,H-CrO1+20.00%CrO,H-CrO1+20.00%CrO,H-CrO1+20.00%CrO,H-CrO1+20.00%CrO,H-CrO1+20.00%CrO,H2.17%CuO1+20.00%CrO,H0.07%CuO1+20.00%CrO,H0.07%CuO1+20.00%CrO,H0.07%CuO1+20.00%CrO,H0.07%CuO1+20.00%CrO,H0.07%CuO1+20.00%CrO,H0.07%CuO1+20.00%CrO,H0.07% </td <td>$Ca(CO3)^0$</td> <td>0.92%</td> <td>$Ca(CO3)^0$</td> <td>0.72%</td>	$Ca(CO3)^0$	0.92%	$Ca(CO3)^0$	0.72%		
Ca(SO4) ⁰ 0.23%Ca(SO4) ⁰ 10.84%Ca ² 89.17%Ca ² 80.15%CaCl ⁺ 0.00%CaCl ⁺ 0.05%CaF ⁺ 0.01%CaF ⁺ 0.01%Cd ⁺² 99.43%Cd ⁺² 93.10%Cd(1 ⁺ 0.13%Cd(1 ⁺ 6.77%Cd(D ⁺) ⁺ 0.13%Cd(C0 <i>y</i>) ⁺ 0.62%Ce(FO <i>x</i>) ⁺² 0.33%Ce(HCO <i>x</i>) ⁺² 0.62%Ce(HCO <i>x</i>) ⁺² 0.33%Ce(HCO <i>x</i>) ⁺² 0.62%Ce ⁺³ 1.58%Ce ⁺³ 1.97%Ce ^{f+2} 0.17%Cef ⁺² 0.22%Co ²⁺² 99.80%Ce ⁺² 99.49%CoCl ⁺ 0.02%CoCl ⁺ 0.35%CoOH ⁺ 0.16%CoOH ⁺ 0.15%Cr0 ² 0.66%Cr0 ² 9.47%Cr0 ² 0.06%Cr0 ² 4.70%Cr0 ¹ 7.86%Cr0 ² -Cr0 ⁴⁺² 100.00%Ca ⁴⁺² 0.07%Cu ⁰⁰ -CuO ⁰ 2.17%Cu0 ⁰ -CuO ⁰ 2.17%Cu0 ⁰ -CuO ⁰ 2.427%Cu0 ¹⁺ 3.36%FeCO ₃ +3.01%FeCO ₃ +6.99%FeHCO ₃ +3.01%FeCO ₃ +6.99%FeHCO ₃ +3.01%GaO ₄ II ⁰ 0.29%FeOH ⁺² 6.874%FeOH ⁺ 0.29%FeOH ⁺² 6.874%FeOH ⁺ 10.08%FeCO ₃ 1.08%GaO ₄ II ⁰ 0.29%FeOH ⁺² 6.874%FeOH ⁺ 10.08%FeO ₃ -8.99%	$Ca(HCO_3)^+$	9.68%	$Ca(HCO_3)^+$	8.23%		
Ca^{1^2} 89.17% Ca^{1^2} 80.15% $CaCl^+$ 0.00% $CaCl^+$ 0.05% Cal^{+2} 99.43% Cal^{+2} 93.10% Cal^+ 0.43% $CalCl^+$ 6.7% $CalCl^+$ 0.43% $CalCl^+$ 6.7% $CalOl^+$ 0.13% $CalOl^+$ 0.11% $Ce(CO_3)^+$ 9.53% $Ce(CO_3)^+$ 0.62% Cel^{+3} 1.5% Ce^{+3} 1.97% Cel^{+2} 0.17% Ce^{+3} 0.22% Ce^{+2} 0.17% Ce^{+3} 0.22% Ce^{+2} 0.17% Ce^{-1} 0.23% Col^+ 0.02% Col^+ 0.35% Col^+ 0.02% Col^+ 0.35% Col^+ 0.02% Col^+ 0.35% Col^+ 0.02% Col^+ 0.25% Col^+ 0.02% Col^+ 0.25% Col^+ 0.02% Col^+	$Ca(SO_4)^0$	0.23%	$Ca(SO_4)^0$	10.84%		
CaCl ⁺ 0.00%CaCl ⁺ 0.01%CaF ⁺ 0.01%CaF ⁺ 0.01%Cd ⁺² 99.43%Cd ⁺² 91.0%CdCl ⁺ 0.13%CdOH ⁺ 0.11%CdOH ⁺ 0.13%CdOH ⁺ 0.11%Ce(CO ₃) ⁺ 97.64%Ce(CO ₃) ⁺² 0.62%Ce ⁺³ 0.53%Ce ⁺¹² 0.22%Ce ⁺² 99.80%Co ⁺² 99.49%Co ⁺² 99.80%Co ⁺² 99.49%CoCl ⁺ 0.02%CoCl ⁺ 0.35%CoOH ⁺ 0.16%CoH ⁺² 9.47%CoQ ⁻¹ 0.06%HcrOa ⁻ 15.30%CrO2 ⁻¹ 0.06%HcrOa ⁻ 15.30%CrO2 ⁻¹ 0.00%CrOH ⁺² 9.93%CsCl ⁰ 100.00%CsCl ⁰ 9.93%CsCl ⁰ -CsCl ⁰ 0.07%CrO2 ⁻¹ 0.06%HcrOa ⁻¹ 15.30%CrO2 ⁻¹ 0.06%HcrOa ⁻¹ 15.30%CrO2 ⁻¹ 0.00%Cs ¹² 9.93%CsCl ⁰ -CsCl ⁰ 0.07%CuOH ⁺² 0.00%Cs ¹² 0.17%CuO ⁰ -CuO ⁰ 24.27%CuOH ⁺ -CuO ¹ 3.36%FeCO ₃ ⁺ 54.47%FeCO ₃ ⁺ 30.17%FeHCO ₃ ⁺ 39.91%GaO ₂ ⁻¹ 8.94%GaO ₄ H ⁰ 0.29%GaO ₂ H ⁰ 0.05%GaO ₄ H ⁰ 0.29%GaO ₂ H ⁰ 10.29%	Ca^{+2}	89.17%	Ca^{+2}	80.15%		
CaF+0.01%CaF+0.01%Cd^{+2}99.43%Cd^{+2}93.10%CdC1+0.43%CdC1+6.77%CdOH+0.13%CdOH+0.11%Ce(CO_2)+0.13%Ce(CO_3)+20.62%Ce(CO_3)+20.53%Ce(HCO_3)+20.62%Ce(HCO_3)+20.53%Ce(HCO_3)+20.22%Ce^{+3}1.58%Ce^{+3}1.97%CeF+20.17%CeF+20.22%CoC1+0.02%CoC1+0.35%CoC1+0.02%CoC1+0.53%CoOH+0.16%CoOH+0.15%CrO+88.99%CrO_7^284.70%CrO_2^0.06%HcrO_4^-1.5.30%CrO_H+23.09%CrOH+2-CsC100.00%CsC10-CrOH+2100.00%CsC10-CsC10-CsC100.07%CuO1+10.00%CsC1024.27%CuO1+100.00%Cs+26.1.7%CuO1+100.00%Cs+26.1.7%CuO1+100.00%Cs+26.1.7%CuO1+13.67%FeCO_31.0.8%FeCO_36.99%FeHCO_3+3.0.17%FeHCO_3+3.4.4%FeCO_31.0.8%FeHCO_3+6.9.9%FeHCO_3+6.3.4%FeHCO_3+6.9.9%FeHCO_3+6.3.4%FeHCO_3+6.9.9%FeHCO_3+6.3.4%FeHCO_3+6.9.9%FeHCO_3+6.3.4% <trr>FeHCO_3+6.9.9%FeHCO_3+6</trr>	$CaCl^+$	0.00%	$CaCl^+$	0.05%		
Cd^{+2} 99.43% Cd^{+2} 93.10% $CdCl^+$ 0.43% $CdCl^+$ 6.77% $CdOH^+$ 0.13% $CdOH^+$ 0.11% $Ce(CO_3)^+$ 97.64% $Ce(CO_3)^+$ 97.10% $Ce(HO_3)^{+2}$ 0.53% $Ce(HO_3)^{+2}$ 0.62% Ce^{+3} 1.58% Ce^{+3} 1.97% Ce^{+2} 0.17% Ce^{+2} 0.22% Co^{+2} 99.80% Co^{+2} 99.49% $CoCl^+$ 0.02% $CoCl^+$ 0.35% CoP^+ 0.02% $CoCl^+$ 0.35% CoP_+ 0.06% $CoOH^-$ 0.15% CrO_2^- 0.66% CrO_4^- 84.70% CrO_2^+ 3.09% CrO_1^+ - CrO_1^+ 0.00% Cs^+ 99.93% Csd^0 - $CsCl^0$ 0.07% CuO^+^2 100.00% Cu^+^2 62.17% CuO^+ 100.00% Cu^+^2 62.17% $CuOH^+$ - $CsCl^0$ 0.07% CuO^+ - $CuOH^+$ 13.36% $FeCO_3$ 6.69% $FeHCO_3^+$ 30.17% $FeCO_3^+$ 54.47% Fe^+^2 68.74% $FeCH^+^2$ 0.29% $FeOH^+^2$ 0.01% GaO_2^- 89.91% GaO_2^- 89.69% Go_2H^0 10.29% $FeCD_3^-$ 45.95%	CaF ⁺	0.01%	CaF^+	0.01%		
CdCl ⁺ 0.43%CdCl ⁺ 6.77%CdOH ⁺ 0.13%CdOH ⁺ 0.11%Ce(CO ₂) ⁺ 97.64%Ce(CO ₂) ⁺ 97.10%Ce(HO ₃) ⁺² 0.53%Ce(HO ₃) ⁺² 0.62%Ce ⁺³ 1.58%Ce ⁺² 0.22%Co ⁺² 99.80%Ce ⁺² 99.49%CoCl ⁺ 0.02%CoCl ⁺ 0.35%CoOH ⁺ 0.16%CoOH ⁺ 0.15%CrO ⁻ 0.06%CrO ₄ ⁻² 84.70%CrO ⁻ 0.06%CrO ₄ ⁻² 84.70%CrO ¹⁺ 3.09%CrOH ⁺² -CrO ¹⁺² 3.09%CrOH ⁺² -CrO ¹⁺² 3.09%CrOH ⁺² -CrO ¹⁺² 100.00%Cs ⁺¹ 99.93%CsCl ⁰ -CsCl ⁰ 0.07%Cu ⁺² 100.00%Cu ⁺² 62.17%CuO ¹⁺² 3.09%CrOH ⁺² 62.17%CsCl ⁰ -ScCl ⁰ 0.07%Cscl ⁰ -CsCl ⁰ 0.07%CuO ¹⁺² 100.00%Cu ¹⁺² 62.17%CuO ¹⁺¹ 3.09%CuO ¹⁺¹ 13.36%FeCO ₃ 6.69%FeHCO ₃ ⁺ 30.17%FeCO ₃ 6.69%FeHCO ₃ ⁺ 0.17%FeHCO ₃ ⁺¹ 3.8.44%FeCO ₃ 1.08%Fe ⁺² 54.47%Fe ⁺² 68.74%FeH ⁺¹ 0.08%GaO ₂ T ⁻⁰ 89.69%GaO ₂ H ⁰ 10.08%GaO ₂ H ⁰ 10.29%Cu10.08%GaO ₂ H ⁰ 10.29%Cu10.08%GaO ₂ H ⁰ 1	Cd^{+2}	99.43%	Cd^{+2}	93.10%		
CdOH+0.13%CdOH+0.11% $Ce(CO_3)^+$ 97.64% $Ce(CO_3)^+$ 97.10%Ce(HCO_3)^{+2}0.53%Ce(HCO_3)^{+2}0.62%Ca^{+3}1.5%Ce^{+3}1.97%CeF^{+2}0.17%CeF^{+2}0.22%Ca^{+2}99.80%CaCl^+0.35%CoCl^+0.02%CoCl^+0.35%CoOH+0.16%CoOH^+0.15%CrOt^-88.99%CrO_4^{-2}84.70%CrO_2^-0.06%HerO_4^-15.30%CrO2H7.86%CrO_3H-CrOH^+23.09%CrOH^+2-CsCl0.000%CsCl99.33%CsCl-CsCl0.07%CuOH-CuO0.07%CuO+2100.00%Cu+20.07%CuO+3-CuO24.27%CuO+4-CuO24.27%CuO+5-CuO24.27%CuO+5-CuO+53.01%FeCO_36.69%FeHCO_3+3.01%FeHCO_3+634.44%FeCO_31.08%FeHCO_3+73.44%FeCO_31.08%FeHC+254.47%Fe+268.74%FeHT+10.29%GaO_2^-69.94%GaO_2T10.08%GaO_4P10.29%FeH264.74%69.94%FaO+210.08%GaO_4P10.29%FaO+210.08%GaO_4P10.29%FaO+210.08%GaO_4P10.29%FaO+2 <td>CdCl⁺</td> <td>0.43%</td> <td>$CdCl^+$</td> <td>6.77%</td>	CdCl ⁺	0.43%	$CdCl^+$	6.77%		
Ce(CO ₃) ⁺¹ 97.64%Ce(CO ₃) ⁺² 97.10%Ce(HCO ₃) ⁺² 0.53%Ce(HCO ₃) ⁺² 0.62%Ce ⁺³ 1.58%Ce ⁺³ 1.97%CeF ⁺² 0.17%CeF ⁺² 0.22%Co ⁺² 99.80%Co ⁺² 99.40%CoCl ⁺ 0.02%CoCl ⁺ 0.35%CoOH ⁺ 0.02%CoOH ⁺ 0.15%CrO ⁺ 88.99%CrO ₄ ⁻² 84.70%CrO ⁺ 0.06%HerO ₄ ⁻² 84.70%CrO2 ⁻ 0.06%CrO2H-CrO1 ⁺² 3.09%CrO2H ⁺² -CrO1 ⁺² 3.09%CrO1H ⁺² -CrO1 ⁺² 0.00%CsCl ⁰ O0.07%Csc ¹⁰ 0.00%CsCl ⁰ O0.07%CuO ⁰ -CuO ⁰ 24.27%CuO ⁰ -CuO ¹ 1.3.6%FeCO ₃ 6.69%FeHCO ₃ ⁺¹ 30.17%FeHCO ₃ ⁺¹ 38.44%FeCO ₃ 1.08%FeV ⁺² 54.47%Fe ¹² 68.74%FeOH ⁺¹ 0.29%GaO ₂ T ⁻⁰ 89.91%GaO ₂ T ⁰ 89.91%GaO ₂ H ⁰ 10.29%	CdOH ⁺	0.13%	CdOH ⁺	0.11%		
Ce(HCO3) ⁺² 0.53% Ce(HCO3) ⁺² 0.62% Ce ⁺³ 1.58% Ce ⁺³ 1.97% CeF ⁺² 0.17% CeF ⁺² 0.22% Co ⁺² 99.80% Co ⁺² 99.49% CoCl ⁺ 0.02% CoCl ⁺ 0.35% CoOH ⁺ 0.16% CoOH ⁺ 0.15% CrO ⁻¹ 0.06% CrO ₄ ⁻² 84.70% CrO ₂ ⁻¹ 0.66% HcrO ₄ ⁻² 84.70% CrO ₂ ⁻¹ 0.06% HcrO ₄ ⁻² 84.70% CrO ₂ ⁻¹ 0.06% KrO ₄ ⁻² 9.93% CrO ₂ ⁻¹ 0.00% CrO ₄ ⁻¹ .5.30% CrO ₂ H 7.86% CrO ₄ H ⁻² - Cs ⁺¹ 100.00% Cs ⁺¹ 9.93% CsCl ⁰ - CsCl ⁰ 0.07% Cu ⁺² 100.00% Cs ⁺² 62.17% CuO ⁰ - CsCl ⁰ 0.07% CuO ¹ - Statt 3.36% FeCO ₃ 6.69% FeHCO ₃ ⁺¹ 3.17% Fe ¹ 2 54.47% Fe ²	$Ce(CO_3)^+$	97.64%	$Ce(CO_3)^+$	97.10%		
Ce^{+3} 1.58% Ce^{+3} 1.97% CeF^{+2} 0.17% CeF^{+2} 0.22% Co^{+2} 99.80% Co^{+2} 99.49% $CoCl^+$ 0.02% $CoCl^+$ 0.35% $CoOH^+$ 0.16% $CoOH^+$ 0.15% CrO^+ 88.99% CrO_4^{-2} 84.70% CrO_2^- 0.06% $HcrO_4^-$ 15.30% CrO_2H 7.86% CrO_2H - $CrOH^{+2}$ 3.09% $CrOH^{+2}$ - $CrOH^{+2}$ 3.09% $CrOH^{+2}$ - Cs^+ 100.00% Cs^+ 99.93% $CsCl^0$ - $CsCl^0$ 0.07% Cu^{+2} 100.00% Cu^{+2} 62.17% CuO^0 - CuO^0 24.27% CuO^0 - $CuOH^+$ 13.36% $FeCO_3$ 6.69% $FeHCO_3^+$ 30.17% $FeHCO_3^+$ 38.44% $FeCO_3$ 1.08% $FeOH^+$ 0.29% $FeHH^{+2}$ 0.01% GaO_2^- 89.91% GaO_2^- 89.69% GaO_2H^0 10.08% GaO_2H^0 10.29% $ HgCl_2^0$ 45.99% $FeSPH^0$	$Ce(HCO_3)^{+2}$	0.53%	$Ce(HCO_3)^{+2}$	0.62%		
CeF^{+2} 0.1% CeF^{+2} 0.22% Co^{+2} 99.80% Co^{+2} 99.49% CoCl ⁺ 0.02% $CoCl^+$ 0.35% CoOH ⁺ 0.16% $CoOH^+$ 0.15% CrO^+ 88.99% CrO_4^{-2} 84.70% CrO_2^- 0.06% $HcrO_4^ 15.30\%$ CrO2H 7.86% CrO_2H $-$ CrOH ⁺² 3.09% $CrOH^{+2}$ $-$ CrOH ⁺² 3.09% $CrOH^{+2}$ $-$ CrOl ⁻¹ 10.00% $CsCl^0$ 0.07% CsCl ⁰ $ CsCl^0$ 0.07% Cu ⁰ $ CuO^0$ 24.27% CuO ⁰ $ CuO^0$ 24.27% CuOH ⁺ $ CuO^+$ 30.17% FeHCO ₃ ⁺ 38.44% FeCO ₃ ⁺ 30.17% FeHCO ₃ ⁺ 54.47% 68.74% FeOH ⁺ 0.29% $6aO_2^ 89.91\%$ GaO_2 ⁻¹ 89.91% $GaO_2^ 89.69\%$ GaO_2 ⁻¹ 10.08% $GaO_2^ 89.69\%$ $ HgCl_0^0$ 10.29%	Ce ⁺³	1.58%	Ce ⁺³	1.97%		
Co^{+2} 99.80% Co^{+2} 99.49% $CoCl^+$ 0.02% $CoCl^+$ 0.35% $CoOH^+$ 0.16% $CoOH^+$ 0.15% CrO^+ 88.99% CrO_4^{-2} 84.70% CrO_2^- 0.06% $HcrO_4^-$ 15.30% CrO_2H 7.86% CrO_2H - $CrOH^{+2}$ 3.09% $CrOH^{+2}$ - $CrOH^{+2}$ 100.00% Cs^+ 99.93% $CsCl^0$ - $CsCl^0$ 0.07% Cu^{+2} 100.00% Cu^{+2} 62.17% CuO^0 - CuO^0 24.27% CuO^0 - CuO^0 3.36% $FeCO_3$ 6.69% $FeHCO_3^+$ 30.17% $FeHCO_3^+$ 38.44% $FeCO_3$ 1.08% $FeOH^+$ 0.29% $FeOH^{+2}$ 0.01% GaO_2^- 89.91% GaO_2^- 89.69% GaO_2H^0 10.08% GaO_2H^0 10.29%	CeF ⁺²	0.17%	CeF^{+2}	0.22%		
CoCl ⁺ 0.02%CoCl ⁺ 0.35%CoOH ⁺ 0.16%CoOH ⁺ 0.15%CrO ⁺ 88.99%CrO ₄ ⁻² 84.70%CrO ₂ ⁻ 0.06%HcrO ₄ ⁻² 15.30%CrO ₂ H7.86%CrO ₂ H-CrOH ⁺² 3.09%CrOH ⁺² -Cs ⁺ 100.00%Cs ⁺ 99.93%CsCl ⁰ -CsCl ⁰ 0.07%Cu ⁺² 100.00%Cu ⁺² 62.17%CuO ⁰ -CuO ⁰ 24.27%CuO ¹ -CuO ⁰ 3.36%FeCO ₃ 6.69%FeHCO ₃ ⁺ 30.17%FeHCO ₃ ⁺ 38.44%FeCO ₃ 1.08%FeOH ⁺ 0.29%FeOH ⁺² 0.01%GaO ₂ ⁻ 89.91%GaO ₂ ⁻ 89.69%GaO ₂ H ⁰ 10.08%GaO ₂ H ⁰ 10.29%	Co^{+2}	99.80%	Co^{+2}	99.49%		
$CoOH^+$ 0.16% $CoOH^+$ 0.15% CrO_{7}^{-} 88.99% CrO_{4}^{-2} 84.70% CrO_{2}^{-} 0.06% $HcrO_{4}^{-}$ 15.30% $CrO_{2}H$ 7.86% $CrO_{2}H$ $ CrOH^{+2}$ 3.09% $CrOH^{+2}$ $ Cs^+$ 100.00% Cs^+ 99.93% $CsCl^0$ $ CsCl^0$ 0.07% Cu^{+2} 100.00% Cu^{+2} 62.17% CuO^0 $ CuO^0$ 24.27% CuO^0 $ CuO^0$ 24.27% CuO^+ 6.69% $FeHCO_3^+$ 30.17% $FeCO_3$ 6.69% $FeHCO_3^+$ 30.17% $FeHCO_3^+$ 38.44% $FeCO_3$ 1.08% $FeOH^+$ 0.29% $FeOH^{+2}$ 0.01% GaO_2^{-} 89.91% GaO_2^{-} 89.69% GaO_2H^0 10.08% GaO_2H^0 10.29%	CoCl ⁺	0.02%	$CoCl^+$	0.35%		
CrO^+ 88.99% CrO_4^{-2} 84.70% CrO_2^- 0.06% $HcrO_4^-$ 15.30% CrO_2H 7.86% CrO_2H $ CrOH^{+2}$ 3.09% $CrOH^{+2}$ $ Cs^+$ 100.00% Cs^+ 99.93% $CsCl^0$ $ CsCl^0$ 0.07% Cu^{+2} 100.00% Cu^{+2} 62.17% CuO^0 $ CuO^0$ 24.27% CuO^0 $ CuO^0$ 24.27% $CuOH^+$ $ CuOH^+$ 13.36% $FeCO_3$ 6.69% $FelCO_3^+$ 30.17% $FelCO_3^+$ 38.44% $FeCO_3$ 1.08% $FeOH^+$ 0.29% $FeOH^{+2}$ 0.01% $GaO_2^ 89.91\%$ $GaO_2^ 89.69\%$ GaO_2H^0 10.08% GaO_2H^0 10.29% $ HgCl_2^0$ 45.99%	CoOH ⁺	0.16%	$CoOH^+$	0.15%		
$CrO_2^ 0.06\%$ $HrO_4^ 15.30\%$ CrO_2H 7.86% CrO_2H $ CrOH^{+2}$ 3.09% $CrOH^{+2}$ $ Cs^+$ 100.00% Cs^+ 99.93% $CsCl^0$ $ CsCl^0$ 0.07% Cu^{+2} 100.00% Cu^{+2} 62.17% CuO^0 $ CuO^0$ 24.27% CuO^0 $ CuO^0$ 24.27% $CuOH^+$ $ CuOH^+$ 13.36% $FeCO_3$ 6.69% $FeHCO_3^+$ 30.17% $FeHCO_3^+$ 38.44% $FeCO_3$ 1.08% $FeOH^+$ 0.29% $FeOH^{+2}$ 0.01% $GaO_2^ 89.91\%$ $GaO_2^ 89.69\%$ GaO_2H^0 10.08% GaO_2H^0 10.29%	CrO^+	88.99%	CrO_4^{-2}	84.70%		
CrO2H7.86%CrO2H-CrOH+23.09%CrOH+2- Cs^+ 100.00% Cs^+ 99.93%CsCl0-CsCl00.07% Cu^{+2} 100.00% Cu^{+2} 62.17%CuO0-CuO024.27%CuOH+-CuOH+13.36%FeCO36.69%FeHCO3+30.17%FeHCO3+38.44%FeCO31.08%FeOH+0.29%FeOH+268.74%GaO2^-89.91%GaO2^-89.69%GaO2H010.08%GaO2H010.29%-HgCl2045.99%	$\mathrm{CrO_2}^-$	0.06%	$HcrO_4^-$	15.30%		
$CroH^{+2}$ 3.09% $CroH^{+2}$ $ Cs^+$ 100.00% Cs^+ 99.93% $CsCl^0$ $ CsCl^0$ 0.07% Cu^{+2} 100.00% Cu^{+2} 62.17% CuO^0 $ CuO^0$ 24.27% $CuOH^+$ $ CuOH^+$ 13.36% $FeCO_3$ 6.69% $FeHCO_3^+$ 30.17% $FeHCO_3^+$ 38.44% $FeCO_3$ 1.08% $FeOH^+$ 0.29% $FeOH^{+2}$ 0.01% $GaO_2^ 89.91\%$ $GaO_2^ 89.69\%$ GaO_2H^0 10.08% GaO_2H^0 10.29%	CrO ₂ H	7.86%	CrO ₂ H	_		
Cs^+ 100.00% Cs^+ 99.93% $CsCl^0$ $ CsCl^0$ 0.07% Cu^{+2} 100.00% Cu^{+2} 62.17% CuO^0 $ CuO^0$ 24.27% CuO^+ $ CuOH^+$ 13.36% $FeCO_3$ 6.69% $FeHCO_3^+$ 30.17% $FeHCO_3^+$ 38.44% $FeCO_3$ 1.08% Fe^{+2} 54.47% Fe^{+2} 68.74% $FeOH^+$ 0.29% $FeOH^{+2}$ 0.01% $GaO_2^ 89.91\%$ $GaO_2^ 89.69\%$ GaO_2H^0 10.08% GaO_2H^0 10.29%	CrOH ⁺²	3.09%	CrOH ⁺²	_		
$CsCl^0$ $ CsCl^0$ 0.07% Cu^{+2} 100.00% Cu^{+2} 62.17% CuO^0 $ CuO^0$ 24.27% $CuOH^+$ $ CuOH^+$ 13.36% $FeCO_3$ 6.69% $FeHCO_3^+$ 30.17% $FeHCO_3^+$ 38.44% $FeCO_3$ 1.08% Fe^{+2} 54.47% $FeOH^{+2}$ 68.74% $FeOH^+$ 0.29% $FeOH^{+2}$ 0.01% $GaO_2^ 89.91\%$ $GaO_2^ 89.69\%$ GaO_2H^0 10.08% GaO_2H^0 10.29%	Cs^+	100.00%	Cs^+	99.93%		
Cu^{+2} 100.00% Cu^{+2} 62.17% CuO^0 - CuO^0 24.27% $CuOH^+$ - $CuOH^+$ 13.36% $FeCO_3$ 6.69% $FeHCO_3^+$ 30.17% $FeHCO_3^+$ 38.44% $FeCO_3$ 1.08% Fe^{+2} 54.47% Fe^{+2} 68.74% $FeOH^+$ 0.29% $FeOH^{+2}$ 0.01% GaO_2^- 89.91% GaO_2^- 89.69% GaO_2H^0 10.08% GaO_2H^0 10.29%	CsCl ⁰	_	CsCl ⁰	0.07%		
CuO^0 $ CuO^0$ 24.27% $CuOH^+$ $ CuOH^+$ 13.36% $FeCO_3$ 6.69% $FeHCO_3^+$ 30.17% $FeHCO_3^+$ 38.44% $FeCO_3$ 1.08% Fe^{+2} 54.47% Fe^{+2} 68.74% $FeOH^+$ 0.29% $FeOH^{+2}$ 0.01% $GaO_2^ 89.91\%$ $GaO_2^ 89.69\%$ GaO_2H^0 10.08% GaO_2H^0 10.29% $ HgCl_2^0$ 45.99%	Cu^{+2}	100.00%	Cu^{+2}	62.17%		
CuOH ⁺ - CuOH ⁺ 13.36% FeCO ₃ 6.69% FeHCO ₃ ⁺ 30.17% FeHCO ₃ ⁺ 38.44% FeCO ₃ 1.08% Fe ⁺² 54.47% Fe ⁺² 68.74% FeOH ⁺ 0.29% FeOH ⁺² 0.01% GaO ₂ 89.91% GaO ₂ 89.69% GaO ₂ H ⁰ 10.08% GaO ₂ H ⁰ 10.29%	CuO ⁰	_	CuO^0	24.27%		
FeCO3 6.69% $FeHCO3^+$ 30.17% FeHCO3^+ 38.44% $FeCO3$ 1.08% Fe^{+2} 54.47% Fe^{+2} 68.74% FeOH^+ 0.29% $FeOH^{+2}$ 0.01% $GaO2^ 89.91\%$ $GaO2^ 89.69\%$ GaO2H0 10.08% $GaO2H0$ 10.29% - $HgCl20$ 45.99%	CuOH ⁺	_	$CuOH^+$	13.36%		
FeHCO3+38.44%FeCO31.08% Fe^{+2} 54.47% Fe^{+2} 68.74%FeOH+0.29%FeOH^{+2}0.01% GaO_2^- 89.91% GaO_2^- 89.69%GaO_2H^010.08% GaO_2H^0 10.29%-HgCl2045.99%	FeCO ₃	6.69%	FeHCO ₃ ⁺	30.17%		
Fe^{+2} 54.47% Fe^{+2} 68.74%FeOH ⁺ 0.29%FeOH ⁺² 0.01% GaO_2^- 89.91% GaO_2^- 89.69% GaO_2H^0 10.08% GaO_2H^0 10.29%-HgCl2045.99%	FeHCO ₃ ⁺	38.44%	FeCO ₃	1.08%		
FeOH+ 0.29% FeOH+2 0.01% $GaO_2^ 89.91\%$ $GaO_2^ 89.69\%$ GaO_2H^0 10.08% GaO_2H^0 10.29% -HgCl2045.99\%	Fe^{+2}	54.47%	Fe^{+2}	68.74%		
GaO_2^- 89.91% GaO_2^- 89.69% GaO_2H^0 10.08% GaO_2H^0 10.29% - $HgCl_2^0$ 45.99%	FeOH ⁺	0.29%	FeOH ⁺²	0.01%		
GaO_2H^0 10.08% GaO_2H^0 10.29% - $HgCl_2^0$ 45.99%	GaO_2^-	89.91%	GaO_2^-	89.69%		
- HgCl ₂ ⁰ 45.99%	GaO_2H^0	10.08%	GaO_2H^0	10.29%		
	_		HgCl ₂ ⁰	45.99%		

Table 2 Migration forms of microelements in Kyiv well rooms using the results of thermodynamic modeling (according to data from 2007 to2012) (Zlobina 2013)

Table 2 continued

Element migration form Percentage Element migration form - HgO^0 K^+ 99.99% K^+ $K(SO_4)^-$ 0.01% $K(SO_4)^ La(CO_3)^+$ 95.52% $La(CO_3)^+$ $La(HCO_3)^{+2}$ 1.20% $La(HCO_3)^{+2}$ $La(SO_4)^+$ 0.06% $La(SO_4)^+$ La^{+3} 3.00% La^{+3} $Li(SO_4)^-$ 0.03% $Li(SO_4)^ Li^+$ 99.96% Li^+ Mg(CO_2)^0 0.71% Mg(CO_2)^0	Dercentage	
$ HgO^0$ K^+ 99.99% K^+ $K(SO_4)^-$ 0.01% $K(SO_4)^ La(CO_3)^+$ 95.52% $La(CO_3)^+$ $La(HCO_3)^{+2}$ 1.20% $La(HCO_3)^{+2}$ $La(SO_4)^+$ 0.06% $La(SO_4)^+$ La^{+3} 3.00% La^{+3} $Li(SO_4)^-$ 0.03% $Li(SO_4)^ Li^+$ 99.96% Li^+ Mg(CO_2)^0 0.71% Mg(CO_2)^0	Percentage	
K^+ 99.99% K^+ $K(SO_4)^-$ 0.01% $K(SO_4)^ La(CO_3)^+$ 95.52% $La(CO_3)^+$ $La(HCO_3)^{+2}$ 1.20% $La(HCO_3)^{+2}$ $La(SO_4)^+$ 0.06% $La(SO_4)^+$ La^{+3} 3.00% La^{+3} $Li(SO_4)^-$ 0.03% $Li(SO_4)^ Li^+$ 99.96% Li^+ Mg(CO_2)^00.71%Mg(CO_2)^0	53.93%	
$K(SO_4)^ 0.01\%$ $K(SO_4)^ La(CO_3)^+$ 95.52% $La(CO_3)^+$ $La(HCO_3)^{+2}$ 1.20% $La(HCO_3)^{+2}$ $La(SO_4)^+$ 0.06% $La(SO_4)^+$ La^{+3} 3.00% La^{+3} $Li(SO_4)^ 0.03\%$ $Li(SO_4)^ Li^+$ 99.96% Li^+ $Mg(CO_2)^0$ 0.71% $Mg(CO_2)^0$	99.28%	
$La(CO_3)^+$ 95.52% $La(CO_3)^+$ $La(HCO_3)^{+2}$ 1.20% $La(HCO_3)^{+2}$ $La(SO_4)^+$ 0.06% $La(SO_4)^+$ La^{+3} 3.00% La^{+3} $Li(SO_4)^-$ 0.03% $Li(SO_4)^ Li^+$ 99.96% Li^+ Mg(CO_2)^00.71%Mg(CO_2)^0	0.72%	
La(HCO3)^{+2}1.20%La(HCO3)^{+2}La(SO4)^+0.06%La(SO4)^+La^{+3}3.00%La^{+3}Li(SO4)^-0.03%Li(SO4)^-Li^+99.96%Lt^+Mg(CO2)^00.71%Mg(CO2)^0	91.17%	
La(SO ₄) ⁺ 0.06% La(SO ₄) ⁺ La ⁺³ 3.00% La ⁺³ Li(SO ₄) ⁻ 0.03% Li(SO ₄) ⁻ Li ⁺ 99.96% Li ⁺ Mg(CO ₂) ⁰ 0.71% Mg(CO ₂) ⁰	1.34%	
La^{+3} 3.00% La^{+3} $Li(SO_4)^-$ 0.03% $Li(SO_4)^ Li^+$ 99.96% Li^+ Mg(CO_2)^0 0.71% Mg(CO_2)^0	3.61%	
Li(SO ₄) ⁻ 0.03% Li(SO ₄) ⁻ Li^+ 99.96% Li^+ Mg(CO ₂) ⁰ 0.71% Mg(CO ₂) ⁰	3.61%	
Li^+ 99.96% Li^+ Mg(CO ₂) ⁰ 0.71% Mg(CO ₂) ⁰	1.88%	
$Mg(CO_2)^0$ 0.71% $Mg(CO_2)^0$	98.10%	
	0.52%	
$Mg(HCO_3)^+$ 12.03% $Mg(HCO_3)^+$	9.56%	
Mg^{+2} 86.81% Mg^{+2}	72.89%	
$MgCl^+$ 0.01% $MgCl^+$	0.08%	
MgF^+ 0.07% MgF^+	0.06%	
MgOH ⁺ 0.01% MgOH ⁺	0.01%	
$MgSO_4^0$ 0.38% $MgSO_4^0$	16.89%	
$Mn(CO_2)^0$ 20.03% $Mn(CO_2)^0$	17.27%	
$Mn(HCO_2)^+$ 30.99% $Mn(HCO_2)^+$	29.17%	
$Mn(SO_4)^0 \qquad 0.09\% \qquad Mn(SO_4)^0$	4.74%	
Mn^{+2} 48.86% Mn^{+2}	48.58%	
$MnCl^+$ 0.01% $MnCl^+$	0.19%	
$HmoQ_4^ 0.11\%$ $HmoQ_4^-$	0.12%	
$M_0 Q_4^{-2}$ 99.89% $M_0 Q_4^{-2}$	99.88%	
$Na(CO_2)^-$ 0.02% $Na(CO_2)^-$	0.02%	
$Na(HCO_2)^0$ 0.82% $Na(HCO_2)^0$	0.79%	
$Na(SO_4)^-$ 0.01% $Na(SO_4)^-$	0.76%	
Na ⁺ 99.14% Na ⁺	98.40%	
NaCl ⁰ – NaCl ⁰	0.03%	
NbO ₂ 45 54% NbO ₂	43.90%	
NbO_2H^0 54.46% NbO_2H^0	56.10%	
Ni(SO,) ⁰ 0.19% Ni(SO,) ⁰	9 52%	
N_{i}^{+2} 87 39% N_{i}^{+2}	81.08%	
Ni($(CO_2)^0$ 4 60% Ni($(CO_2)^0$	3 17%	
$N_{1}(EO_{3})^{+}$ 632% $N_{1}(EO_{3})^{+}$	5 38%	
NiOH ⁺ 0.50% NiOH ⁺	0.31%	
Pb^{+2} 9.90% Pb^{+2}	12 04%	
PbO 0.03% PbC1 ⁺	0.20%	
$PbOH^+$ 90.07% $PbOH^+$	87 72%	
$S_{\rm CO}^+$ 10.73% $S_{\rm CO}^+$	12 51%	
$s_{cO_{a}}^{-}$ 0.21% $s_{cO_{a}}^{-}$	0.21%	
$S_{1}CO_{2}H^{0}$ 89.06% $S_{1}CO_{2}H^{0}$	87.28%	
SnO_2^0 81 43% SnO_2^0	83 74%	
$\sin O_2^{-2}$ 0.02% $\sin O_2^{-2}$	0.01%	
SnO ₃ H ⁻ 18 55% SnO ₃ H ⁻	16 25%	
$Sr(CO_2)^0$ 0.24% $Sr(CO_2)^0$	0.20%	
$Sr(HCO_2)^+$ $SO(2770)$ $Sr(HCO_2)^+$	7 10%	
$Sr(SO_4)^0$ 0.14% $Sr(SO_4)^0$	6.98%	

Table 2 continued

Cenomanian-Callovian groundwater complex		Bajocian aquifer			
Element migration form	Percentage	Element migration form	Percentage		
<i>Sr</i> ⁺²	91.60%	Sr^{+2}	85.68%		
VO^+	97.85%	$H_2 VO_4^{-}$	84.75%		
VOH ⁺²	0.07%	HVO_4^{-2}	15.21%		
VO^{+2}	0.04%	VO^{+2}	_		
VOOH ⁺	1.49%	$\rm VOOH^+$	_		
$H_2VO_4^-$	0.47%	$H_2VO_4^-$	_		
Y^{+3}	78.41%	Y^{+3}	80.61%		
YO ⁺	0.52%	YO^+	0.42%		
YOH ⁺²	21.07%	YOH^{+2}	18.97%		
$Yb(CO_3)^+$	99.52%	$Yb(CO_3)^+$	99.29%		
Yb ⁺³	0.24%	YbF ⁺²	0.11%		
YbF ⁺²	0.10%	YbF ⁺²	_		
Zn^{+2}	80.77%	Zn^{+2}	82.34%		
ZnO	0.02%	$ZnCl^+$	0.12%		
ZnOH ⁺	19.19%	ZnOH^+	17.51%		
ZrO_2^0	8.17%	$\operatorname{ZrO_2}^0$	9.14%		
ZrO_3H^-	91.81%	ZrO_3H^-	90.84%		

point of view, a method for determining the values of the lower limit of biologically significant concentrations in potable water is presented. The lower limit of biologically significant concentration (LLBSC) is the value at which the intake of an element into the body with potable water is 5% of the total average statistical intake. At the same time, it is considered that approximately 2 L of potable water are consumed.

According to this method, heavy metals, and essential and rare elements biologically significant concentration (BSC) of the studied waters were calculated (Table 3). The elements whose content is higher than the BSC and can affect the microelement balance of a human are established: Ba, Fe, Sc, Sr, Y. It is important to point out that not only the excess but also the lack of microelements (Zn, Cu, F, Se, K) in the studied waters can cause specific diseases in the body, trace element diseases (Zlobina 2013).

During 2020–2022, the authors conducted a similar study for another large hydrogeological structure of Ukraine, AS of Ukrainian Shield (Koshliakova et al. 2022). This structure marks by the letter A in Fig. 1. In contrast to the Dnieper–Donetsk AS, no interlayer waters were studied, but the first aquifer from the surface (aquifer in fractured zone of crystalline rocks and their weathering crust, PR1), which is used by the rural areas' inhabitants for potable water supply. The results are presented in Table 4.

The comparison of the BSC's with the content of microelements and individual elements determined during

the research made it possible to reveal an excess of such elements as Sr and Ba in the studied potable water. Cr is present in sufficient quantity. Meanwhile, insufficient amounts of elements such as V, Mn, Co, Ni, Cu, Zn, Cd, and Pb were established.

During the three monitoring years (2020–2022), the concentration of such elements as V, Cr, Mn, Co, Ni, Zn, Sr, Ba, Cd, and Pb remains relatively stable. Instead, the concentration of Li increased more than 10 times in the observed water intake facilities, and as of 2022, the concentration of this element in well waters corresponds to the BSK value.

According to the authors, the assessment of the balanced level of the mineral composition of water from the sources of centralized water supply is extremely important from the point of view of the ecological assessment of potable groundwater. According to Safranov et al. (2016), if individual chemical elements are considered as sanitary and toxicological indicators of potable water safety and quality, then the range of their optimal values does not always correspond to the normative values of indicators of the physiological completeness of potable water mineral composition.

Although the BSC's values of mineral components of potable water and their lower limits may not be sufficiently substantiated, they provide an opportunity to expand the list of criteria for assessing the level of potable waterbalanced mineral composition. This issue is relevant

Table 3 BSC for interlayer waters used for potable water supply of the population of Kyiv

Element, mg/L	State standard of Ukraine (7525:2014); Sanitary Rules of Ukraine (2.2.4-171-10)	USEPA	EU	BSC	Cenomanian- Callovian groundwater complex		Bajocian aquifer	
					Mean	Maximum	Mean	Maximum
Ba	0.1	2	_	0.02	0.03	0.24	0.1	0.86
Be	0.0002	0.004	_	0.00025	0.00002	0.00034	-	-
V	-	_	_	0.025	0.0008	0.013	0.0014	0.01
Bi	-	_	_	0.00025	0.0002	0.003	0.0007	0.002
С	-	_	_	7500	2.2	5.8	1.6	4.4
Fe	0.2	_	0.2	0.45	0.19	0.73	0.25	1.62
Y	0.05	_		0.0004	0.00075	0.0034	0.0006	0.001
Cd	-	0.005	0.005	0.0025	0.00008	0.00008	_	-
Κ	0.001	_	_	62.5	7.9	14.71	12.9	17.3
Ca	130	_	_	27.5	77	119	44	94
Co	0.1	_	_	0.0075	0.00006	0.001	0.0003	0.0014
Si	10	_	_	0.25	8.4	14.2	3.4	10.5
Li	-	_	_	0.025	0.0034	0.014	0.008	0.022
Mg	80	_	_	7.5	15.8	37	30	18.7
Mn	0.05	_	0.05	0.05	0.032	0.25	0.05	0.26
Cu	1.0	1.3	2.0	0.025	0.002	0.075	0.002	0.0084
Мо	0.07	_	_	0.00625	0.0007	0.014	0.0009	0.02
As	0.01	0.01	0.01	0.00125	0.00001	0.006	_	_
Na	200	_	200	112.5	15.35	147.35	38	247
Ni	0.02	_	0.02	0.0075	0.0008	0.02	0.0008	0.05
Nb	-	_	_	0.0065	0.00033	0.0008	0.00031	0.0007
Sn	_	_	_	0.075	0.0003	0.0005	_	_
Hg	0.0005	0.002	0.001	0.00037	0.00004	0.00005	0.00004	0.00006
Pb	0.01	0.015	0.01	0.01	0.00047	0.008	0.00055	0.002
Se	0.01	0.05	0.02	0.00175	0.00016	0.0002	_	_
Ag	0.025	_	_	0.00125	0.0003	0.008	0.0006	0.002
Sc	_	_	_	0.000001	0.00058	0.0014	0.00069	0.0013
Sr	7.0	_	_	0.05	0.39	0.84	0.45	1.1
SO_4	250	_	250	_	0.5	37.1	2.47	53
Ti	-	_	_	0.02	0.011	0.019	0.007	0.17
F	1.5	_	_	0.05	0.3	0.61	0.19	1.0
Cl	250	_	_	100	4.7	56.8	8.9	257.4
Cr	0.05	_	_	0.00175	0.002	0.01	0.003	0.002
Zn	1.0	_	_	0.3	0.017	0.28	0.015	0.07
Zr	-	_	_	0.05	0.007	0.05	0.009	0.029

because long-term consumption of potable water, characterized by an imbalance in its mineral composition, can be one of the negative factors affecting the population's health. Therefore, there is a need for further special studies. As a result of such studies, recommendations can be made regarding the need to adjust the diet of local inhabitants due to the additional use of vitamin–mineral complexes or, in the case of detection of excess concentrations of vital elements, regarding appropriate water treatment measures. Moreover, such studies have scientific value, as they can serve as a basis for performing biogeochemical regionalization with an outline of possible risks to public health in connection with the geochemical features of environmental

 Table 4 Generalized results of trace element analysis of water from the aquifer in the fractured zone of crystalline rocks and their weathering crust (AS of Ukrainian Shield) with the BSC's indication

Element, mg/L	Type of water intake facilities						
	Shaft			Well			
	2020	2021	2022	2020	2021	2022	
Li	0.000922	0.004662	0.008828	0.001555	0.004949	0.02495	0.025
V	0.001036	0.001099	0.00074	0.000122	0.000209	0.00012	0.025
Cr	0.003326	0.004038	0.00228	0.001729	0.002891	0.00208	0.00175
Mn	0.000824	0.004389	0.00067	0.000633	0.002043	0.000592	0.05
Co	0.000008	0.000131	0.00004	0.000017	0.00014	0.00006	0.0075
Ni	0.000211	0.015931	0.001005	0.000864	0.017301	0.0009	0.0075
Cu	0.000197	0.001318	0.0013345	0.012659	0.018194	0.00817	0.025
Zn	0.009309	0.091527	0.037095	0.023665	0.074792	0.04425	0.3
Sr	0.312244	0.386823	-	0.178328	0.21342	-	0.05
Cd	0.000023	0.000101	0.00005	0.000081	0.000055	0.00005	0.0025
Ba	0.063614	0.080914	-	0.065276	0.085503	-	0.02
Pb	0.000085	0.000906	0.000255	0.000249	0.001582	0.00024	0.01

The number of samples: 25

components, one of which is natural potable waters (Koshliakova 2022).

6 Conclusions

As a result of the research, it was revealed that the elevated (compared to the background values) indicators of the studied interlayer waters' geochemical state, spatially gravitate to the right-bank part of the city and the Dnieper River valley. This fact is consistent with modern ideas about groundwater protection, based on the geomorphological zoning of the territory. The achieved results demonstrate the sustainable environmental impact of changes in the hydrodynamic and hydrogeochemical conditions of active water exchange zone aquifers inherited during maximum water intake.

Comparative analysis revealed a tendency to decrease hydrogen carbonates and increase chlorides and sulfates in the Cenomanian-Callovian groundwater complex, whereas the cation composition remains relatively stable. The authors explain this by the fact that in the process of longterm exploitation of aquifers, powerful depression funnels were formed, which caused pore solutions to be squeezed out of relatively water-resistant rocks. When these solutions transfer to deep interlayer groundwaters, they change their composition. In addition, the processes of ion exchange, and processes of precipitation of montmorillonite and illite, accompanied by the removal of sodium from water, play a major role. Thus, the presence of a stable man-made factor (long-term water intake with the depression funnels formation), and the weak protection of the Cenomanian-Callovian groundwater complex in comparison with the Bajocian aquifer, determine the differences in the dynamics of changes in the chemical composition of the studied interlayer waters over time.

Microelement concentrations in the studied interlayer waters are similar to the distribution in hydrocarbonatecalcium natural waters of other hydrogeological systems of Ukraine and correspond to those of Clark concentrations for freshwater aquifer complexes of sedimentary rocks. The average concentration of heavy metals in the Bajocian aquifer is higher than in the overlying Cenomanian-Callovian groundwater complex. It is most likely can be connected with a natural factor which is in the waterbearing rocks of the Bajocian aquifer, there are lenses of brown coal (black lignite), which can potentially contain impurities of heavy metals in its composition. Also, according to the authors, lead can come as a result of upward filtration from the aquifer in the deposits of Dronivska and Serebryanska formations of the Lower Triassic, which lies at a depth of 300-350 m and is characterized by varied chemical composition.

Calculated BSCs of heavy metals, essential and rare elements of the studied waters made it possible to detect the excess (Ba, Fe, Sc, Sr, Y) and the deficiency (Zn, Cu, F, Se, K) of certain trace elements. According to the authors, the BSC's values of mineral components of potable water and their lower limits provide an opportunity to expand the list of criteria for assessing the level of potable waterbalanced mineral composition.

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Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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