# Long-term fluctuations in the chemical composition of surface waters and climate change

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## SUMMARY

The aim of the study was to identify trends in long-term changes in the chemical composition of river waters using the example of river basins in Ukraine and their possible relationship with climate change. We used long-term observational data on the chemical composition of water (main ions and mineralization) of the Western Bug (1961-2018) and Southern Bug (1951-2018) rivers. Three characteristic periods are distinguished for these rivers: the first period is reference; the second period is transformational, characterized by a process of increasing water mineralization; the third period is modern, characterized by a process of certain stabilization of the hydrochemical regime of rivers. As a result of climate change, the share of underground river nutrition is increasing. It is known that groundwater has a higher mineralization, which leads to an increase in the mineralization of river water.

## Introduction

Currently, it is recognized that climatic changes are occurring on the planet, affecting not only air temperature, but also the mode of precipitation. In this regard, the question is being raised about the study of possible changes in the water balance of water bodies, and, in wider prospective, the amount of water resources in various regions and countries. However, up to date, the question of the relationship between water quality and climate change remains in the background. The change of hydrological conditions in the river basins will affect the chemical composition and quality of natural waters, as well as the possibilities of maintaining the stability of freshwater ecosystems. The UNESCO International Hydrological Program has created a platform for scientific cooperation in the monitoring and assessment of changes in water resources due to climate change. The question of research on changes in the quality of water resources is also raised there (Addressing, 2015). There are publications on the impact of climate change on surface water quality relative to the production of drinking water (*Delpla et al., 2009*).
Issues of the impact of climate change on the chemical composition of surface water in Ukraine at this stage are little developed. Among the publications on this subject, the following can be noted (*Khil`chevskij, Kurilo, 2015; Loboda, Pylypiuk, 2017; Osadchyi, 2017*).

## Methods of research

In this work, we used long-term observational data on the chemical composition of river waters along the rivers Western Bug (1961-2018) and Southern Bug (1951-2018). The Southern Bug River basin is located entirely in Ukraine (No.4), the Western Bug River is transboundary and belongs to the Vistula basin (No.6) - Figure 1. To assess the quantitative changes in the water mineralization value, it is proposed to use the coefficient of halinity $K_G = G/G_f$, where G is the mineralization of water in the modern period, mg·dm$^{-3}$; $G_f$ - mineralization of water for the period of the conditional hydrochemical background, mg·dm$^{-3}$.
The aim of the study was to identify trends in long-term changes in the chemical composition of river waters using the example of river basins in Ukraine and their possible relationship with climate change.

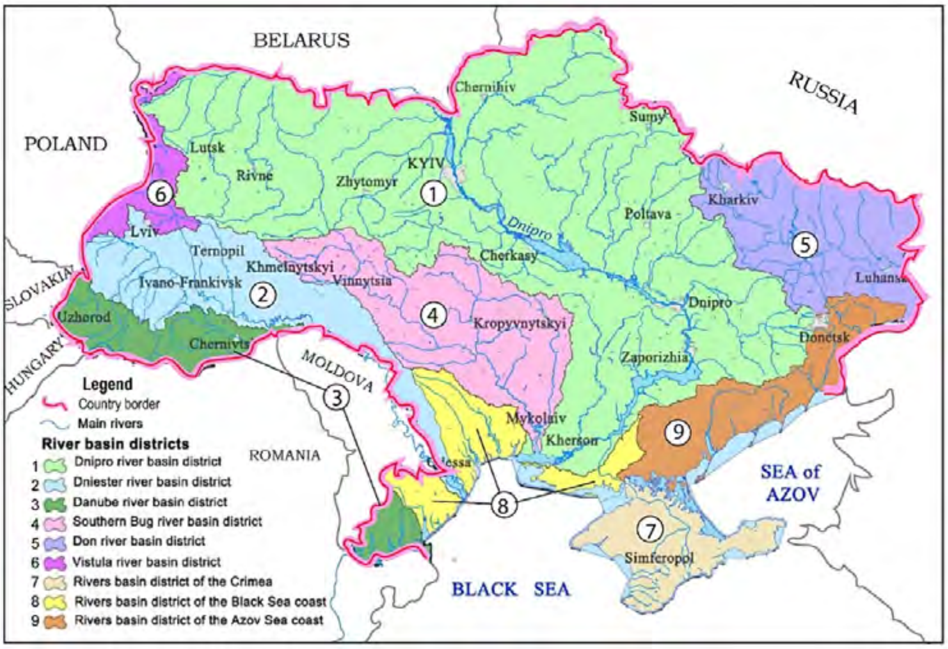


***Figure 1*** *The Southern Bug River Basin (4) and the Western Bug River (6) on the map of the hydrographic zoning of Ukraine*

**Results**

The chemical composition of water in many rivers of Ukraine (according to the values of water salinity and the content of major ions) is subject to transformation both under the influence of anthropogenic load and as a result of the influence of natural factors, in particular, fluctuations in the water content of rivers, which is associated with climatic changes. As shown by studies of climatic characteristics, as well as their impact on the nature of the formation of river flow, there is a significant change in the annual distribution of river water flow in Ukraine. This is manifested in a decrease in the volume of surface water runoff during the spring flood (which is associated with a decrease in snow reserves in the catchment areas in winter due to frequent thaws) and an increase in the role of underground nutrition at this time (*Khil`chevskij, Kurilo, 2015*).

*1. Western Bug River*

The total area of the Western Bug basin is 39420 $km^2$, the length of the river is 772 km. The area of the Western Bug basin in Ukraine is 11205 $km^2$, the length of the river is 404 km, of which 220 km form a border between Ukraine and Poland (*Khilchevskiy et al., 2018; 2019*). It was found that the minimum mineralization values are 388 $mg{\cdot}dm^{-3}$ (1962), and the maximum is 804 $mg{\cdot}dm^{-3}$ (1988). In the long-term prospective, the average annual mineralization values tend to increase (Figure 2).

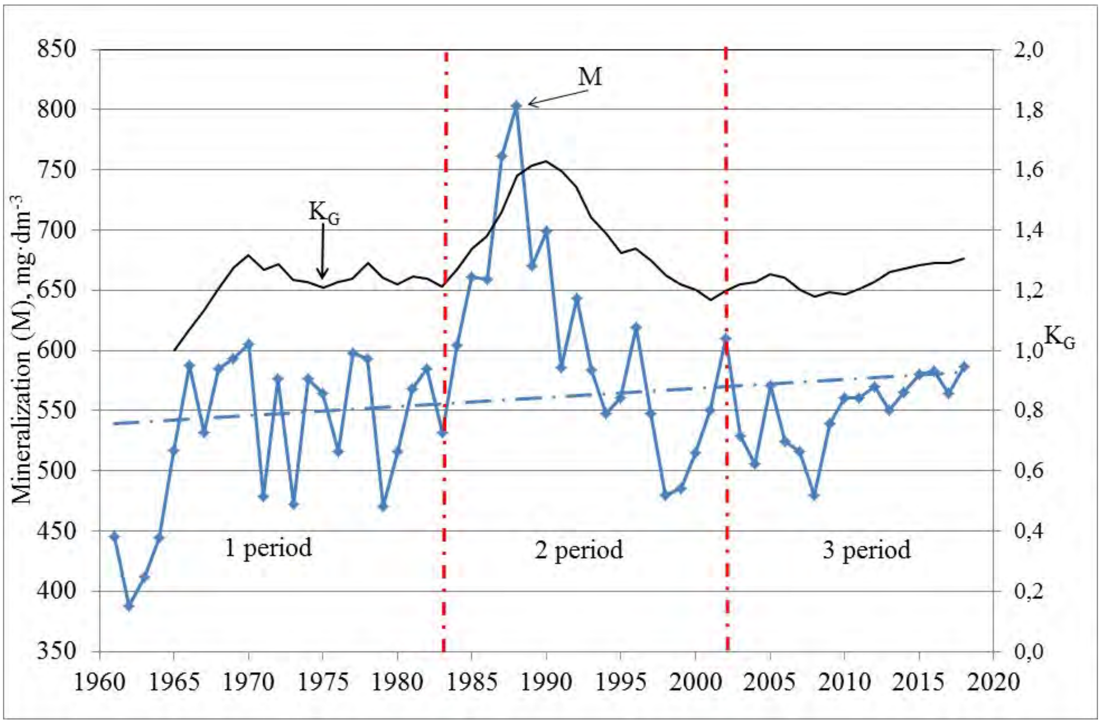


***Figure 2*** *The average annual mineralization of water in the Western Bug River (Kamyanka-Buzka), 1961-2018*

Three characteristic periods can be distinguished in the changes in the mineralization of the water in the Western Bug River: 1 - reference; 2 - transformational, characterized by increased mineralization of water; 3 - modern, characterized by a certain stabilization of the hydrochemical regime of rivers.
The first period (1961-1983) was characterized by low mineralization and a constant calcium bicarbonate composition, $K_G$ values were about 1.0. The second period (transformational, 1983-2002) was characterized by an increase in the mineralization of water and a noticeable change in its composition of the main ions, $K_G$ increased to 1.6. The third period (modern, 2003-2018) is characterized by stabilization of the hydrochemical regime of the river ($K_G$ - 1.3-1.4).
*2. South Bug River*

The Southern Bug River has a basin area of 63700 km² and a length of 806 km. It was established that the minimum mineralization values are 390 mg·dm$^{-3}$ (1960), and the maximum is 762 mg·dm$^{-3}$ (1992). In the long-term prospective, the average annual mineralization values tend to increase (Figure 3).

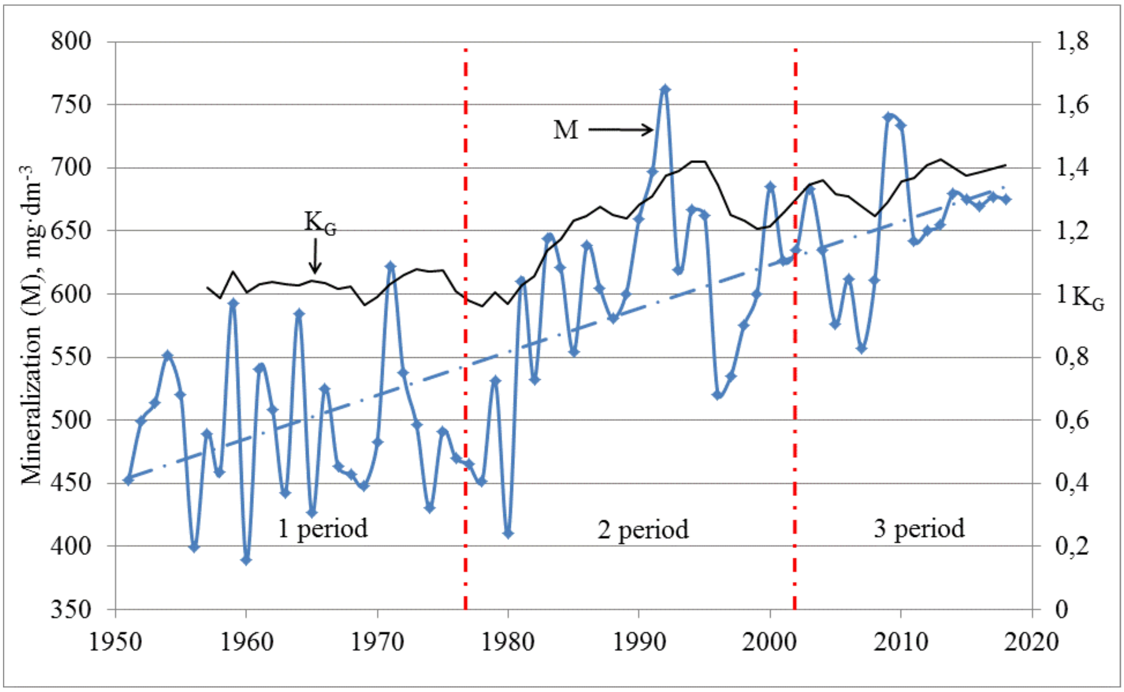


***Figure 3*** *The average annual mineralization of water in the South Bug River (Oleksandrivka), 1951-2018*

***Table 1*** *The volume of underground runoff and water mineralization Southern Bug (Oleksandrivka)*

| Years | Groundwater flow | | Mineralization water, mg·dm$^{-3}$ |
|---|---|---|---|
| | км$^3$ | % | |
| 1951 | 0.70 | 35.1 | 452.7 |
| 1957 | 0.79 | 36 | 545.5 |
| 1985 | 2.35 | 56.5 | 699.0 |
| 1993 | 0.62 | 50.8 | 620.0 |
| 2009 | 1.05 | 44.2 | 750.5 |
| 2011 | 0.88 | 39.5 | 641.8 |
| 2018 | 0.82 | 41.2 | 675.1 |

Three characteristic periods can be distinguished in the changes in the mineralization of the water in the South Bug River: 1 - reference; 2 - transformational, characterized by increased mineralization of water; 3 - modern, characterized by a certain stabilization of the hydrochemical regime of rivers.
The first period (1951-1977) was characterized by low mineralization and a constant calcium bicarbonate composition, $K_G$ values were about 1.0. The second period (transformational, 1978-2003) was characterized by an increase in the mineralization of water and a noticeable change in its composition of the main ions, $K_G$ increased to 1.6. The third period (modern, 2004-2018) is characterized by stabilization of the hydrochemical regime of the river ($K_G$ - 1.3-1.4).
A correlation dependence was established between the ratio of the share of underground runoff in the total river flow and the amount of river water mineralization (r = 0.7) - Table 1.

## Conclusions

The researches have shown that average annual indicators have a constant upward trend with small cyclical fluctuations. For the Southern Bug River, the average annual mineralization increased from 452 $mg\cdot dm^{-3}$ at the beginning of the observation period in 1951 to 675 $mg\cdot dm^{-3}$ in 2018. The minimum mineralization value is 390 $mg\cdot dm^{-3}$ (1960), and the maximum is 762 $mg\cdot dm^{-3}$ (1992).
For the Western Bug River, the average annual mineralization increased from 445 $mg\cdot dm^{-3}$ at the beginning of the observation period in 1961 to 587 $mg\cdot dm^{-3}$ in 2018.The minimum mineralization value is 388 $mg\cdot dm^{-3}$ (1962), and the maximum is 804 $mg\cdot dm^{-3}$ (1988).

Based on the changes in water mineralization and the coefficient of halinity for the studied rivers, three characteristic periods are distinguished: 1 - reference, $K_G = 1$; 2 - transformational, characterized by increased salinity of water, $K_G = 1\text{-}1.6$; 3 - modern, characterized by a certain stabilization of the hydrochemical regime of rivers, $K_G = 1.3\text{-}1.4$.

A correlation dependence was established between the ratio of the share of underground runoff in the total river flow and the amount of river water mineralization ($r = 0.7$). As a result of climate change, the share of underground river nutrition is increasing. It is known that groundwater has a higher mineralization, which leads to an increase in the mineralization of river water.

The recorded changes in the hydrochemical regime of rivers are the result of climatic changes (water regime in particular).

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