Complex Assessment and Forecasting of Chemical Pollution of Small Rivers by Economic and Mathematical Modelling Methods

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Introduction

Small rivers are the initial link of the river network, and any changes in their regime are undoubtedly reflected throughout the hydrographic chain. Therefore, the current problem of modern hydrochemistry and hydroecology is the assessment of anthropogenic load on small rivers.

The main sources of pollution of reservoirs are industrial and household effluents, with which pesticides, heavy metal ions, etc. are getting into the reservoirs in increasing quantities. Heavy metals belong to the class of conservative contaminants that are not used or decomposed during migration on trophic chains, have mutagenic and toxic effect, significantly reduce the intensity of biochemical processes in aquatic organisms. Some abiotic factors such as changes in acidity, mineralization or water temperature are not less dangerous for the life of hydrobionts.

The purpose of this work

is to determine the hydrochemical parameters of the river Seret water and the features of the accumulation of heavy metals with bivalve molluscs *Unio pictorum L.* to predict the chemical contamination of the reservoir in the near future.

The **Seret River** is the left tributary of the Dniester that flows through the Ternopil Oblast of Ukraine. Its length is 242 km; the basin covers some 3900 km2. The towns of Ternopil, Terebovlia and Chortkiv sit along the river's banks.

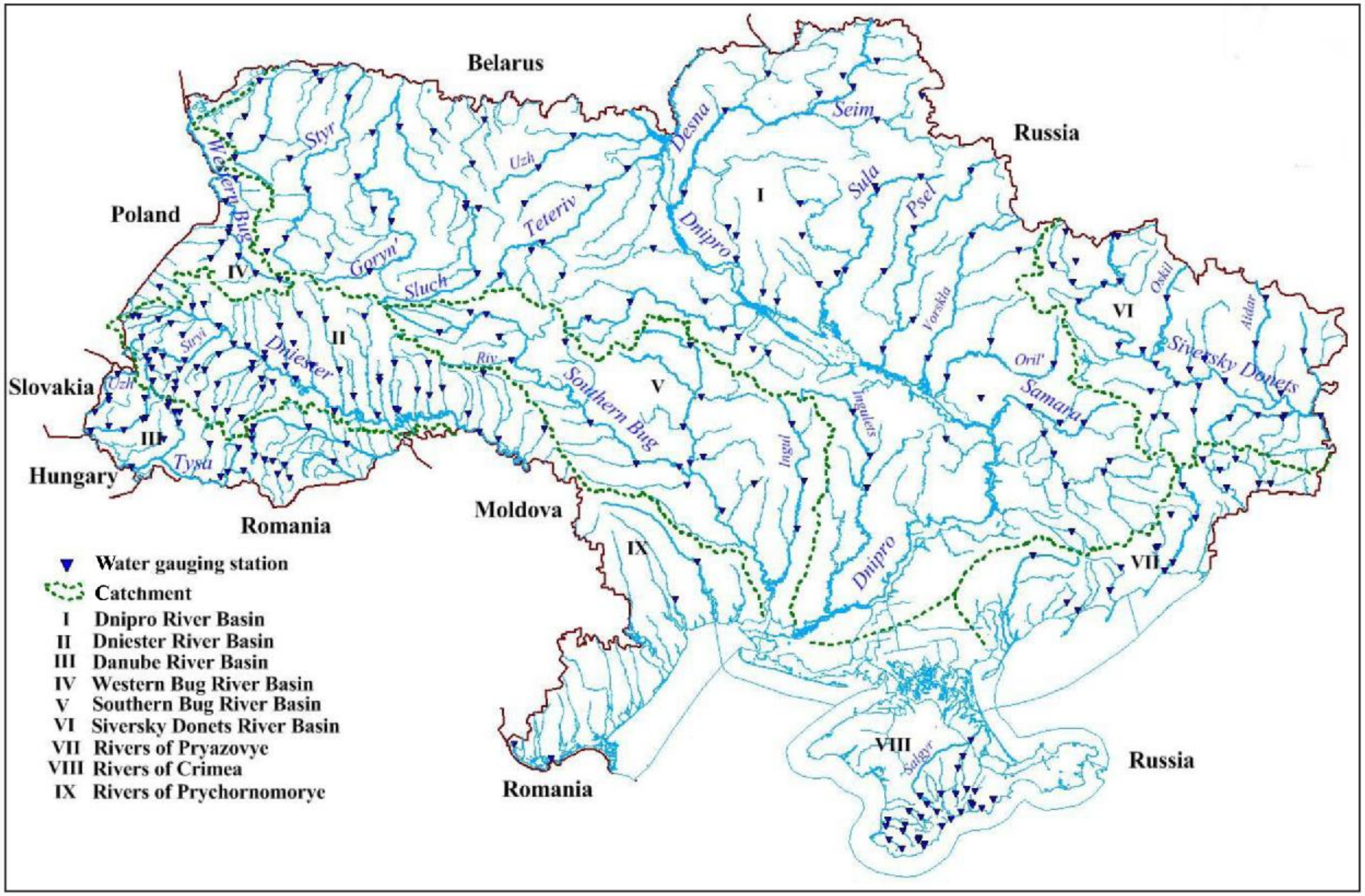


Fig. 1. The main catchments of rivers on the territory of Ukraine

Ternopil Pond, a reservoir set in the center of Ternopil created in the place of swamps on the **river Seret**. Today Ternopil pond is surrounded by a park. It is a favourite walking place of residents and visitors of the city.

Fig. 2. Ternopil Pond

Material and methods of the research

- Water samples for the study were collected in spring (April) and summer (July) from the Seret River at two points: above and below Ternopil city, which gives an opportunity to estimate the level of anthropogenic pressure and chemical pollution of the river.
- The determination of hydrochemical parameters and the content of heavy metals were carried out by conventional methods.
- For studies of metal content and enzyme activity in bivalve mollusc *Unio pictorum* L., we selected the liver and used standard techniques.
- Statistical processing of the obtained data was performed using the “Microsoft Excel” package. Prediction of metal content for the near future was performed using a prediction technique based on Markov chain theory and modern information systems such as Matlab.

1. Analysis of general chemical indicators of water quality

Table 1

Separate hydrochemical parameters of the river Seret (M±m, n=4)

Indicators	Spring		Summer	
	Above Ternopil	Below Ternopil	Above Ternopil	Below Ternopil
pH index	6.80±0.15	7.35±0.10	7.45±0.20	7.50±0.15
Oxygen, mg O_2/dm^3	7.95±0.06	5.73±0.19	6.86±0.22	4.67±0.37
Total hardness of water, *mmol/l*	5.16±0.05	5.58±0.07	6.52±0.04	7.10±0.02
Nitrates (NO_3^-), *mg/l*	6.63±0.12	8.82±0.14	2.63±0.42	5.94±0.15
Nitrites (NO_2^-), *mg/l*	0.03±0.01	0.05±0.02	0.07±0.05	0.14±0.02
Ammonium cations (NH_4^+), *mg/l*	0.09±0.01	0.72±0.03	0.23±0.03	0.92±0.03
Phosphates (PO_4^{3-}), *umol/l*	0.07±0.02	0.20±0.02	0.04±0.01	0.25±0.03
Chlorides (Cl^-), *mg/l*	11.40±0.90	16.55±1.20	28.50±1.60	35.40±0.90
Permanganate oxidation, *mmolO/l*	5.14±0.07	5.42±0.08	5.58±0.07	8.12±0.09

2. Gross metal content in the water of the Seret River

Table 2

Total metal content in the Seret River water (M±m, n=5)

Metal	Spring		Summer	
	Above Ternopil	Below Ternopil	Above Ternopil	Below Ternopil
Zn	0.015±0.006	0.019±0.004	0.020±0.005	0.018±0.002
Mn	0.019±0.003	0.025±0.003	0.023±0.003	0.045±0.003
Cu	0.0008±0.0002	0.0009±0.0002	0.0006±0.002	0.0015±0.001
Pb	0.009±0.002	0.011±0.003	0.009±0.002	0.015±0.002
Cd	0.003±0.001	0.007±0.002	0.007±0.001	0.009±0.002

An increase in the concentration of metals (Mn, Cu and Pb) in the summer below Ternopil may be caused by the discharge of insufficiently treated wastewater.

The series of concentrations of metals in the water of the Seret River is as follows manganese → zinc → plumbum → cadmium → copper.

3. Features of metal accumulation by molluscs

Table 3

The content of metals in the liver of the bivalve mollusc Unio pictorum L. (mg / kg of wet tissue)

Metal	Spring		Summer	
	Above Ternopil	Below Ternopil	Above Ternopil	Below Ternopil
Zn	31,5	32,6	33,7	29,9
Mn	11,5	12,6	13,7	31,9
Cu	1,5	1,2	1,7	3,4
Pb	0,5	0,6	0,7	1,4
Cd	0,55	0,7	0,75	0,8

Table 4

Metal bioaccumulation coefficients by bivalve mollusc
Unio pictorum L.

Metal	Spring		Summer	
	Above Ternopil	Below Ternopil	Above Ternopil	Below Ternopil
Zn	2100	1716	1685	1661
Mn	605	504	595	709
Cu	1875	1333	1833	2266
Pb	56	59	78	93
Cd	183	100	107	89

4. Prediction of bioaccumulation of metals by economic and mathematical modelling methods

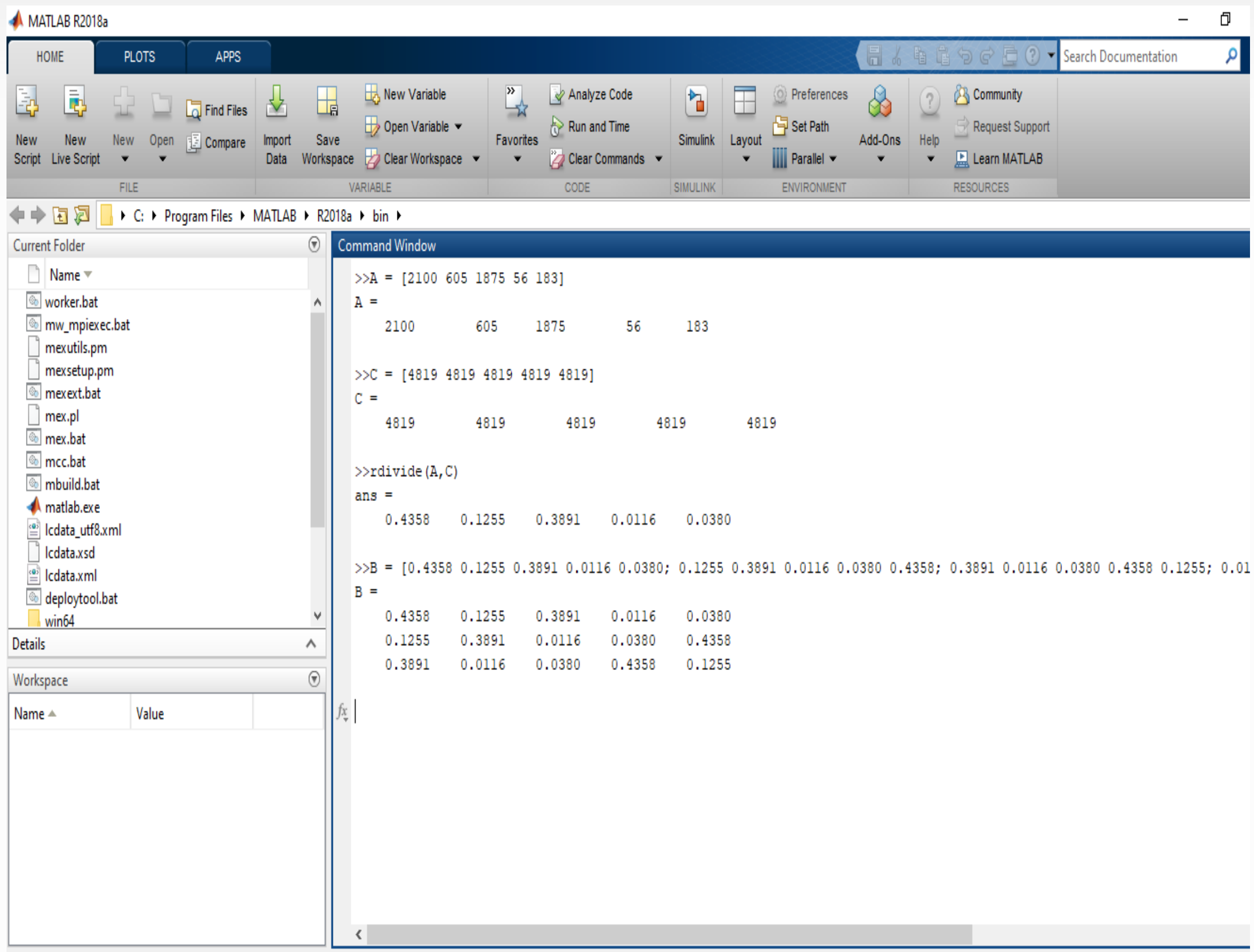


Fig.1. **Visualization of modeling of metal bioaccumulation coefficients based on Markov processes in Matlab software**

Table 5

The results of predicting the bioaccumulation of metals are implemented in Matlab

	P_1	P_2	P_3	P_4	P_5
K = 1	0.4358	0.1255	0.3891	0.0116	0.0380
K = 2	0.3586	0.1250	0.1956	0.1956	0.1250
K = 3	0.2551	0.1579	0.2494	0.1674	0.1702
K = 4	0.2364	0.1769	0.2049	0.2049	0.1769
K = 5	0.2141	0.1858	0.2133	0.1933	0.1936
K = 6	0.2002	0.1933	0.2021	0.2021	0.1933
K = 7	0.2038	0.1957	0.2037	0.1984	0.1984
K = 8	0.2024	0.1981	0.2007	0.2007	0.1981
K = 9	0.2010	0.1988	0.2010	0.1996	0.1996
K = 10	0.2007	0.1995	0.2002	0.2002	0.1995
K = 11	0.2003	0.1997	0.2003	0.1999	0.1999
K = 12	0.2002	0.1999	0.2001	0.2001	0.1999
K = 13	0.2001	0.1999	0.2001	0.2000	0.2000
K = 14	0.2001	0.2000	0.2000	0.2000	0.2000

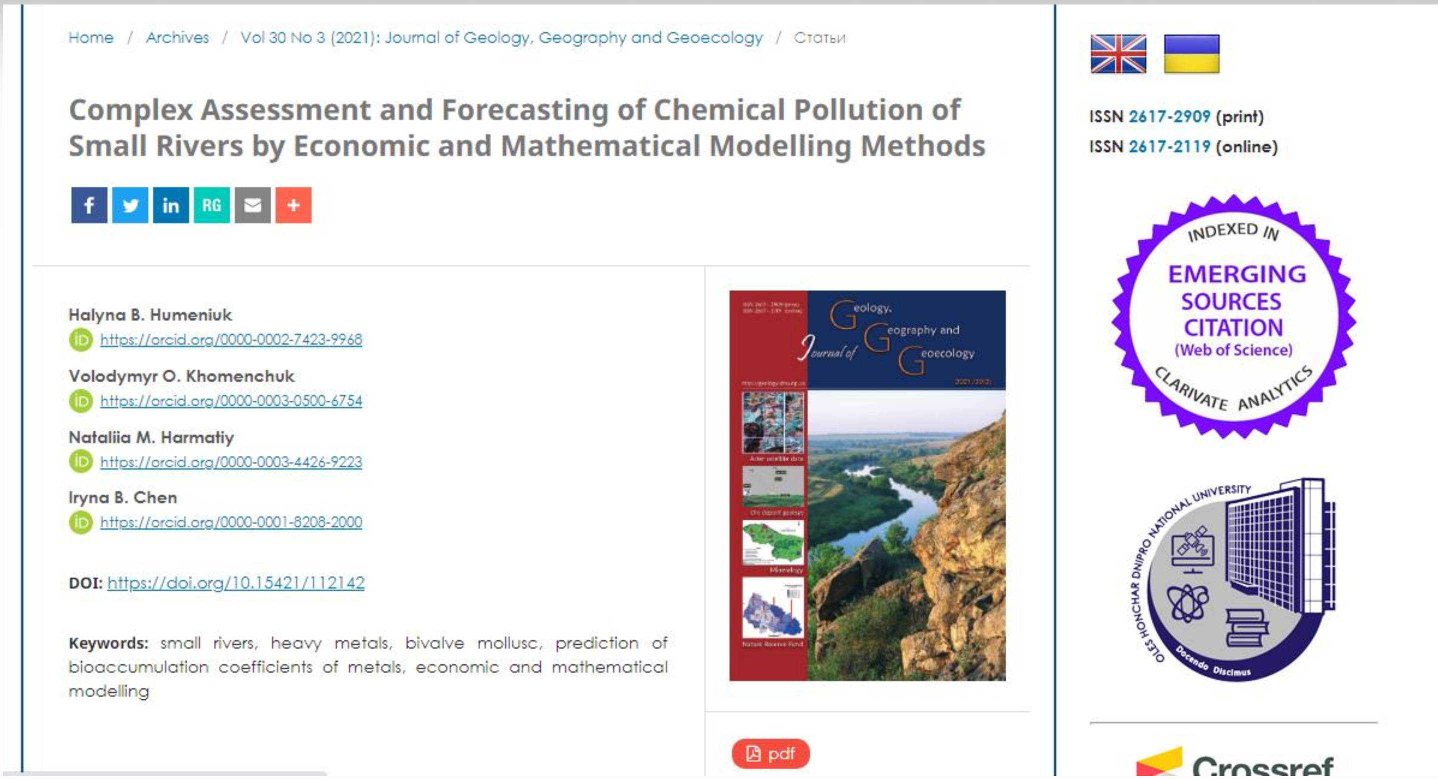
Conclusions

- ✓ The chemical composition of the river Seret waters formed by the influence of a number of factors, but seasonal and anthropogenic factors play a dominant role. In the spring season, a number of hydrochemical indicators (pH, water hardness, concentrations of NO_2^-, NH_4^+, Cl^- and ions metals) have lower values than the summer, which is primarily due to the increase in water level (spring flood).

- ✓ An increase in the concentration of metals (Mn, Cu and Pb) in the summer below Ternopil may be caused by the discharge of insufficiently treated wastewater. The series of concentrations of metals in the water of the Seret River is as follows Mn → Zn → Pb → Cd → Cu.

- ✓ The accumulation of mollusks of heavy metal ions depends on the physical and chemical characteristics of the environment of the aquatic environment. In general, the series of accumulation of metals in the tissues of molluscs *Unio pictorum* L. has the form Zn → Mn → Cu → Pb → Cd, and the coefficients of bioaccumulation of heavy metals have the following form Zn> Cu> Mn> Cd> Pb.

- ✓ Using the economic-mathematical modelling tools and statistical methods made it possible to identify correlations between the studied indicators and to forecast the status of water pollution in the near future.



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Thank you for attention!

Welcome for collaboration

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