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

Halyna B. Humeniuk[1], Volodymyr O. Khomenchuk[1], Nataliia M. Harmatiy[2], Iryna B. Chen[1]

[1]*Ternopil Volodymyr Hnatiuk National Pedagogical University, Ternopil, Ukraine, e-mail:* irynachen35@gmail.com
[2]*Ternopil Ivan Pului National Technical University, Ternopil, Ukrain, e-mail:* garmatiy.nat@meta.ua

Abstract. The purpose of this work is to determine the hydrochemical parameters of the water of the river Seret and the features of the accumulation of heavy metals by bivalve molluscs *Unio pictorum L.* to predict the chemical contamination of the reservoir in the near future. Water samples for the study were taken in spring (April) and summer (July) from the Seret River at two points: above and below Ternopil. It is established that the chemical composition of the water of the river Seret is formed under 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, concentration of NO_2^-, NH_4^+, Cl^- ions and metals) have lower values than in the summer. In addition, there is an increase in the amount of organic matter, ammonium cations, nitrite ions, chloride ions, phosphate ions and a decrease in oxygen concentration below Ternopil, especially in the summer season. This is evidence that the Seret River is under significant anthropogenic impact. An increase in the concentration of metals (Mn, Cu and Pb) in summer below Ternopil was revealed, which may be due to the discharge of insufficiently treated wastewater. The series of metal concentrations in the water of the Seret River looks as follows Mn → Zn → Pb → Cd → Cu, and the series of accumulation of metals in the tissues of molluscs *Unio pictorum* L. has the form Zn → Mn → Cu → Pb → Cd. On the basis of bioaccumulation coefficients of heavy metals by molluscs, a prediction of the situation on their content in water for the short term based on the theory of Markov chains was made. This theory allows us to make forecasts of a factor, taking into account the possibility of accidental influences on the environment, and to investigate the highest probability of finding a factor in a certain numerical parameter. The possibility of using economic and mathematical modelling tools and statistical methods based on correlation-regression analysis using modern Matlab information systems to identify correlations between chemical indicators of water quality and biological molluscs for modelling the environmental situation of the river Seret and assessing the contribution of the studied indicators in pollution of small rivers is shown.

Keywords: small rivers, heavy metals, bivalve mollusc, prediction of bioaccumulation coefficients of metals, economic and mathematical modelling.

Комплексна оцінка та прогнози хімічного забруднення малих річок методами економіко-математичного моделювання

Г. Б. Гуменюк[1], В. О. Хоменчук[1], Н. М. Гарматій[2], І. Б. Чень[1]

[1] *Тернопільський національний педагогічний університет імені Володимира Гнатюка, м. Тернопіль, Україна,*
e-mail: irynachen35@gmail.com
[2] *Тернопільський національний технічний університет імені Івана Пулюя, м. Тернопіль, Україна,*
e-mail: garmatiy.nat@meta.ua

Анотація. Малі річки є початковою ланкою річкової мережі, і всі зміни у їх режимі, безперечно, позначаються на всьому гідрографічному ланцюзі. Тому актуальною проблемою сучасної гідрохімії та гідроекології є оцінка антропогенного навантаження на малі річки України. Метою роботи є визначити гідрохімічні показники води річки Серет та особливості акумуляції важких металів двостулковими молюсками *Unio pictorum* L. для прогнозування хімічного забруднення водойми на найближчу перспективу. Проаналізовано такі гідрохімічні показники: pH, кисень, загальна твердість води, нітрати, нітрити, катіони амонію, фосфати, хлориди, перманганатна окислюваність. Зразки води для дослідження відбирали весною (квітень) та літом (липень) із р. Серет у двох точках: вище і нижче м. Тернопіль, що дало можливість оцінити рівень антропогенного тиску та хімічного забруднення річки. У результаті комплексного гідроекологічного дослідження гідрохімічних показників проведено оцінку якості води річки Серет. Визначено концентрації марганцю, цинку, міді, плюмбуму і кадмію у водоймі та особливості їх накопичення двостулковими молюсками *Unio pictorum* L. Розраховано коефіцієнти біоакумуляції, які відображають відношення вмісту металу в організмі гідробіонта до вмісту його в навколишньому середовищі. Виявлено позитивну кореляцію між вмістом металів в печінці двостулкових молюсків та їх вмістом у воді. На основі коефіцієнтів біоакумуляції важких металів молюсками здійснено прогноз

ситуації по їх вмісту у воді на найближчу перспективу на базі теорії ланцюгів Маркова. Дана теорія дозволяє здійснювати прогнози чинника, враховуючи можливість випадкових впливів на середовище, та досліджує найбільшу ймовірність перебування чинника в певному числовому параметрі. Показано можливість застосування інструментарію економіко-математичного моделювання та статистичних методів на основі кореляційно-регресійного аналізу з використанням сучасних інформаційних систем типу Matlab для виявлення кореляційних зв'язків між хімічних показників якості води та біологічними показниками молюсків для моделювання екологічної ситуації р. Серет та оцінки внеску досліджуваних показників у забруднення малих річок.

Ключові слова: малі річки, важкі метали, молюски, прогнозування коефіцієнтів біоакумуляції металів, економіко-математичне моделювання.

Introduction.

Small rivers contain the bulk of Ukraine's freshwater reserves and play a huge role in the life of the population. According to experts, they form for 60 % of Ukraine's total water resources. 60 % of water resources of these rivers are concentrated in Polissia and Forest-steppe, about 25 % in Carpathians and about 12 % in Steppe (Arsan et al, 2006; Lashko, 2008).

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 of Ukraine (Loucks, 2017).

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 (Arsan et al, 2006). 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 (Abubakar et al, 2015; Malik et al, 2014; Manoj et al, 2012; Mur, 1987). Some abiotic factors such as changes in acidity, mineralization or water temperature are not less dangerous for the life of hydrobionts (Altenburger, R. et al. 2019; Yan, 2015).

Bivalve molluscs are one of the functional units of aquatic ecosystems through which trace elements flow. By the way of nutrition they are referred to as filter feeders. This helps the molluscs to purify water and accumulate various metals, including toxic ones, in soft tissues. The ability of certain species of bivalve molluscs to accumulate high concentrations of metals, availability, prevalence and low migration activity, allows the use the bivalve molluscs as bioindicator organisms (Chapman,1996; Novikov et al, 1990).

In view of the above, 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.

Material and methods of the research.

Water samples for the study were collected in spring (April) and summer (July) 2015 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. After sampling, water samples were recorded and transported to the laboratory for testing. The determination of hydrochemical parameters and the content of heavy metals were carried out by conventional methods (Arsan et al, 2006; Novikov et al, 1990).

For studies of metal content and enzyme activity in bivalve mollusc *Unio pictorum* L., we selected the liver and used standard techniques (Nasrabadi, 2015).

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 (Prystavka, 2017; Rohatynskyi, 2017).

Results and their analysis. 1. Analysis of general chemical indicators of water quality.

We analyzed some of the hydrochemical parameters of the Seret River waters above and below Ternopil city (table 1).

The pH index of the water was the lowest in spring above Ternopil (pH 6.8) and the highest in summer below Ternopil (pH 7.5). According to this indicator, river water can be attributed to neutral waters characterized by the presence of $Ca(HCO_3)_2$, $Mg(HCO_3)_2$.

The oxygen concentrations in the water of the River Seret ranged from 4.67 to 7.95 mg / l. The highest oxygen content was observed in the spring above Ternopil city, and the lowest in the formation below Ternopil city. Probably lower oxygen content in summer is associated with higher organic matter content, as evidenced by the permanganate index.

Water hardness is a property of natural waters that depends on the presence of dissolved salts of calcium and magnesium in it. The highest indicator of total water hardness in the Seret River was observed in summer below Ternopil, the lowest value of total hardness was observed in spring in the area above the city. The water of the Seret River can be attributed to waters of medium hardness.

The maximal concentration of nitrates in water was noted in the spring below Ternopil city. Obviously, NO_3 ions get into surface water as a result of the washing of mineral fertilizers during spring floods. It also should be noted that their inflow with urban wastewater, as evidenced by the increase in their concentration in the stream below Ternopil city.

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

The highest concentration of nitrite ions (0.14 mg / l) was observed below Ternopil in summer. This indicates that the river water is contaminated with wastewater regularly, often municipal wastewater that is not treated sufficiently.

Concentrations of NH_4^+ ions in the water of the River Seret range from 0.09 to 0.92 mg / dm³. It should be noted that in the summer season the concentration of ammonium nitrogen is higher. The study of the content of phosphate ions shows an increase in their quantity below Ternopil and emphasizes the fact of the phosphates supply with wastewater in Ternopil city.

Concentrations of chloride ions range from 11.4 to 35.4 mg / dm³. The tendency of increasing Cl – ions in the summer season is noted. In addition, the increase of the chloride ion fraction from 28.50 mg / dm³ in the Seret River above Ternopil city to 35.4 mg / dm³ in the Seret River – below Ternopil city is clearly visible.

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

We have determined the gross concentrations of manganese, zinc, copper, plumbum and cadmium in the water of the Seret River above and below Ternopil (table 2).

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

The level of zinc in water varies within a fairly narrow water range from 0.025 to 0.030 mg / dm³. However, there may be a risk of accumulation of metal by hydrobionts and their chronic poisoning. Its toxicity is caused by antagonism with other heavy metals.

The concentration of manganese in the water of the river Seret varied from 0.019 to 0.045 mg / dm³. There was a sharp increase in Mn content in the summer below Ternopil. The high content of manganese can be caused by the relatively low oxygen content during this period, which causes the inflow of metal from the

bottom sediments due to recovery (under conditions of oxygen deficiency), the good water solubility of its compounds, their low complexing ability and high migration capacity.

Manganese can pose a significant danger to hydrobionts due to the high mobility of the metal and the relatively high level of "free" ions that have the greatest toxicity.

There is a noticeable increase in the concentration of cuprum in the Seret River basin below Ternopil city during the summer season. Lead content in river water was in the range 0.009–0.015 mg / dm3. The maximal concentration of metal was observed in the summer season in the formation below the city and exceeded the background level by 1.5 times.

The cadmium concentration in the river Seret varied from 0.003 to 0.009 mg / dm^3. The minimal concentration of metal was observed in the spring season above Ternopil, and the maximal – in the summer in the river bed below the city.

In general, the series of metals distribution in the water of the Seret River is as follows Mn → Zn → Pb → Cd → Cu.

3. Features of metal accumulation by mollusks.

Bivalve mollusks are one of the functional parts of aquatic ecosystems through which the flows of microelements pass. According to the method of feeding they are referred to as filters. The mollusk 20–30 mm long passes 1.5–2.0 l of water a day. As a result, mollusks help to purify water and accumulate various metals in soft tissues, including toxic ones (Anawar, 2020).

The penetration of heavy metal ions into the body of aquatic animals and their accumulation depend on many external and internal factors. The molecular mechanisms of this process are still understood poorly. It is only known that in general the penetration of heavy metal ions into the body of aquatic organisms includes the following stages: binding to the mucous epithelium; transport across the apical membrane; penetration of metal through the basolateral membrane, at the level of which the regulation of flow takes place; transportation of metals by blood flow to all parts of the body. The liver, being one of the main organs involved in important metabolic processes, and in which there is a detoxification of a number of harmful substances, is characterized by a high ability to accumulate metals (Neiko, 2003; Khochachka, 2002).

The accumulating ability of hydrobionts is usually expressed by bioaccumulation coefficient (K), which reflect the ratio of metal content in the body to its content in the environment (water, soil):

$$K = Cm / Cw, \qquad (1)$$

where Cm and Cw are the metal concentrations in the mollusc tissues (mg/kg) and the metal concentrations in the water, mg/dm^3. The obtained data made it possible to calculate the bioaccumulation rates of heavy metals by shellfish with respect to water (Nasrabadi, 2015).

Data on the accumulation of individual metals in the liver of bivalve mollusk Unio pictorum L. caught in the River Seret are presented in the table 3.

Table 3. The content of metals in the liver of the bivalve mollusks *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

The analysis of the results indicates a rather high level of zinc accumulation (29.9–33.7 mg / kg) in the liver of molluscs and the absence of seasonal features of the accumulation of this metal in the liver of molluscs. The manganese content was slightly lower compared to zinc. However, a positive correlation should be noted between the concentration of manganese in water and the tissues of *Unio pictorum* L. Thus, the maximal concentrations of Mn in both water and in the liver of mollusks were observed in samples taken from the Seret River below Ternopil.

Our data suggest that increasing the concentration of copper ions in water leads to an increase in their content in the liver of bivalve molluscs. Thus, the maximal amount of metal was accumulated by molluscs caught in the Seret River in the summer below Ternopil. It is obvious that there is a positive correlation between the metal content in water and in the liver of molluscs, which is confirmed by the bioaccumulation coefficient.

The study found a relatively small amount of accumulated lead by the mollusc liver. The metal content ranges from 0.5 to 1.4 mg / kg of wet tissue. It should

be noted, that the increase in the amount of accumulated metal in the summer in molluscs selected below Ternopil, which is confirmed by the coefficient of bioaccumulation (k = 93.3). Obviously, this is due to the inflow of insufficiently treated wastewater into the river.

The analysis of the obtained results showed that the amount of cadmium in the liver of *Unio pictorum* L. tends to increase slightly in molluscs that were caught below Ternopil. The metal content in the liver of aquatic organisms varied in the range of 0.55–0.80 mg / kg, and the bioaccumulation coefficient ranged from 89 to 183.

In general, the series of metal accumulation in the tissues of the molluscs of *Unio pictorum* L. has the following form Zn → Mn → Cu → Pb → Cd. The accumulation of heavy metal ions by molluscs is an active and regulated process, which depends on both the physicochemical features of the environment and the physiological and biochemical activity of the body of the hydrobionts.

The coefficients of heavy metal bioaccumulation are have the following form Zn> Cu> Mn> Cd> Pb (table 4).

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

Consequently, molluscs accumulate significant amounts of metals, and bioaccumulation factors can indicate both the contamination of the environment with these metals and their accessibility to hydrobionts. In general, a positive correlation can be observed between the content of metals in the liver of bivalve molluscs and their content in water.

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

On the basis of the input data presented in table 3, we model the ecological situation based on the theory of Markov chains for the short term. The calculations will be made using Matlab.

Incoming data:

Metal	Zn	Mn	Cu	Pb	Cd
Spring/above Ternopil city	2100	605	1875	56	183

Construct a matrix of metal bioaccumulation coefficients in Matlab.

>>A = [2100 605 1875 56 183]

A =

    2100   605   1875   56   183

Find the sum of the metal bioaccumulation coefficients: 4819

>>C = [4819 4819 4819 4819 4819]

C =

    4819   4819   4819   4819   4819

Find the probabilities (the proportion of metal bioaccumulation coefficients):

>>rdivide(A,C)

ans =

    0.4358 0.1255 0.3891 0.0116 0.0380

Form a transition matrix:

>>B = [0.4358 0.1255 0.3891 0.0116 0.0380; 0.1255 0.3891 0.0116 0.0380 0.4358; 0.3891 0.0116 0.0380 0.4358 0.1255; 0.0116 0.0380 0.4358 0.1255 0.3891; 0.0380 0.4358 0.1255 0.3891 0.0116]

B =

    0.4358 0.1255 0.3891 0.0116 0.0380
    0.1255 0.3891 0.0116 0.0380 0.4358
    0.3891 0.0116 0.0380 0.4358 0.1255
    0.0116 0.0380 0.4358 0.1255 0.3891
    0.0380 0.4358 0.1255 0.3891 0.0116

We will assume that the starting point of time (2015) will be found by system in the state S_0. The probability of the state $p_{(0)} = 1$. Write the vector of initial states $p_{(0)} = (1; 0; 0; 0; 0)$.0.0116 0.0380 0.4358 0.1255 0.3891

    0.0380 0.4358 0.1255 0.3891 0.0116

We will assume that the starting point of time (2015) will be found by system in the state S_0. The probability of the state $p_{(0)} = 1$. Write the vector of initial states $p_{(0)} = (1; 0; 0; 0; 0)$.

The implementation of the simulation will be presented in the Matlab software (Fig. 1).
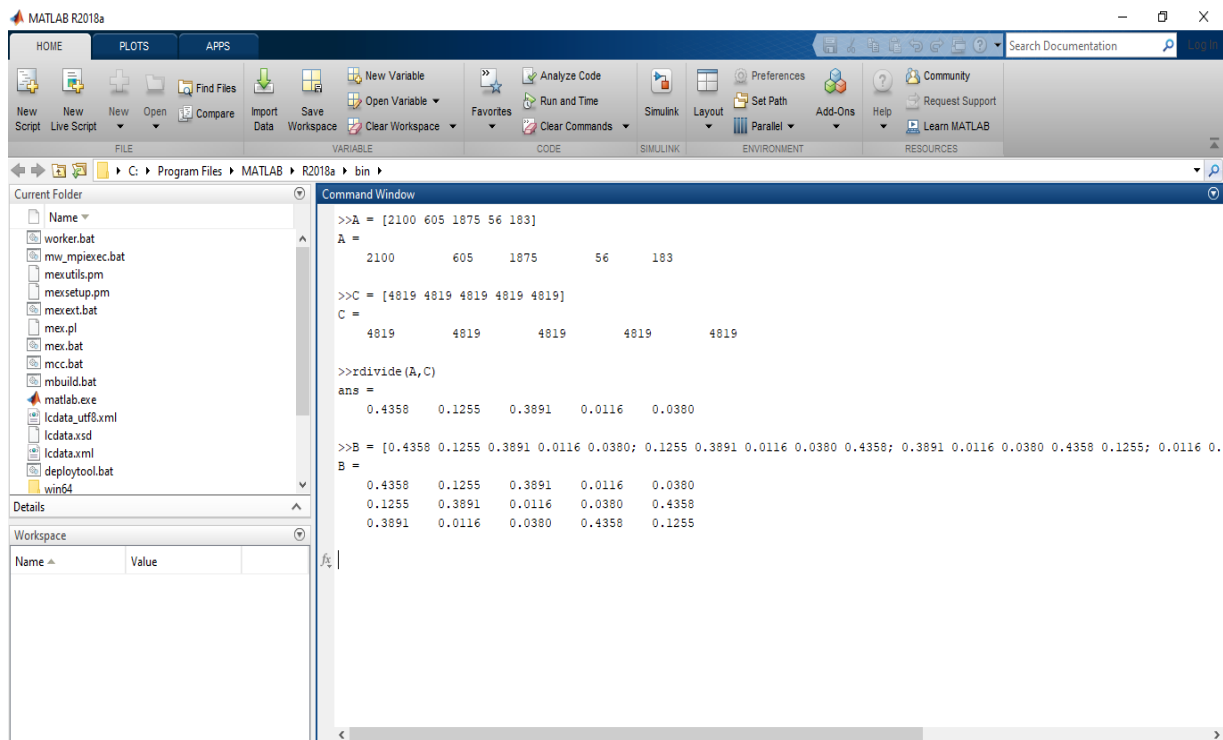
Fig.1. Visualization of modeling of metal bioaccumulation coefficients based on Markov processes in Matlab software.

Now we predict the coefficients of bioaccumulation of metals in the near future. The forecasting data implemented in the Matlab software environment will be written in the table 5.

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

The results show that in the simulation of the ecological situation of metal bioaccumulation by bivalve mollusc *Unio pictorum* L. in water with the biggest probability of 0.44 will be a Zn concentration in the amount of 2100, but we see that after 9 seasons, samples of metals in the studied reservoir with a probability of 0.2 will be the Zn concentration and approximately the same volume will be the concentration of Cu metal in the reservoir, and metals such as Pb and Cd will have approximately the same probability of 0.19, according to the modelling that we presented in the table 5. Next season, the share of Zn in the reservoir will have a probability of 0.2007. In the eleventh and twelfth seasons, the largest share of the metal concentration in the reservoir will have Zn metal, and the smallest will be the concentration of Mn metal in the reservoir. The use of economic and mathematical modelling to predict the concentration of metals in the studied reservoir will prolong the dynamics of previous studies to prognose the results.

465

On the basis of the input data presented in the Table 3, we model the economic situation based on Markov chain theory for the short term and how many years the situation will be stabilize. The calculations will be made using Matlab.

Incoming data:

Metal	Zn	Mn	Cu	Pb	Cd
Summer/above of Ternopil city	1685	595	1833	78	107

Construct a matrix of metal bioaccumulation coefficients in Matlab.

>>A = [1685 595 1833 78 107]

A =

   1685   595   1833   78   107

Form a vector of sums:

>>C = [4298 4298 4298 4298 4298]

C =

   4298   4298   4298   4298   4298

Find the probabilities (the proportion of metal bioaccumulation coefficients):

>>rdivide(A,C)

ans =

   0.3920 0.1384 0.4265 0.0181 0.0249

Form a transition matrix:

>>B = [0.3920 0.1384 0.4265 0.0181 0.0249; 0.1384 0.4265 0.0181 0.0249 0.3920; 0.4265 0.0181 0.0249 0.3920 0.1384; 0.0181 0.0249 0.3920 0.1384 0.4265; 0.0249 0.3920 0.1384 0.4265 0.0181]

B =

   0.3920 0.1384 0.4265 0.0181 0.0249
   0.1384 0.4265 0.0181 0.0249 0.3920
   0.4265 0.0181 0.0249 0.3920 0.1384
   0.0181 0.0249 0.3920 0.1384 0.4265
   0.0249 0.3920 0.1384 0.4265 0.0181

We will assume that the starting point of time (2015) will be found by system in the state S_0. The probability of the state $p_{(0)} = 1$. Write the vector of initial states $p_{(0)} = (1; 0; 0; 0; 0)$.

We now predict the bioaccumulation coefficients of metals until the situation stabilizes.

1 step value:

>>p = [1 0 0 0 0]

p =

   1   0   0   0   0

2 step value:

>>p1 = [p*B]

p1 =

   0.3920 0.1384 0.4265 0.0181 0.0249

3 step value:

>>p2 = [p1*B]

p2 =

   0.3557 0.1312 0.1909 0.1909 0.1312

4 step value:

>>p3 = [p2*B]

p3 =

   0.2457 0.1648 0.2518 0.1669 0.1705

5 step value:

>>p4 = [p3*B]

The fragment of metal bioaccumulation coefficient prediction is shown in the Matlab software environment (Fig. 2).
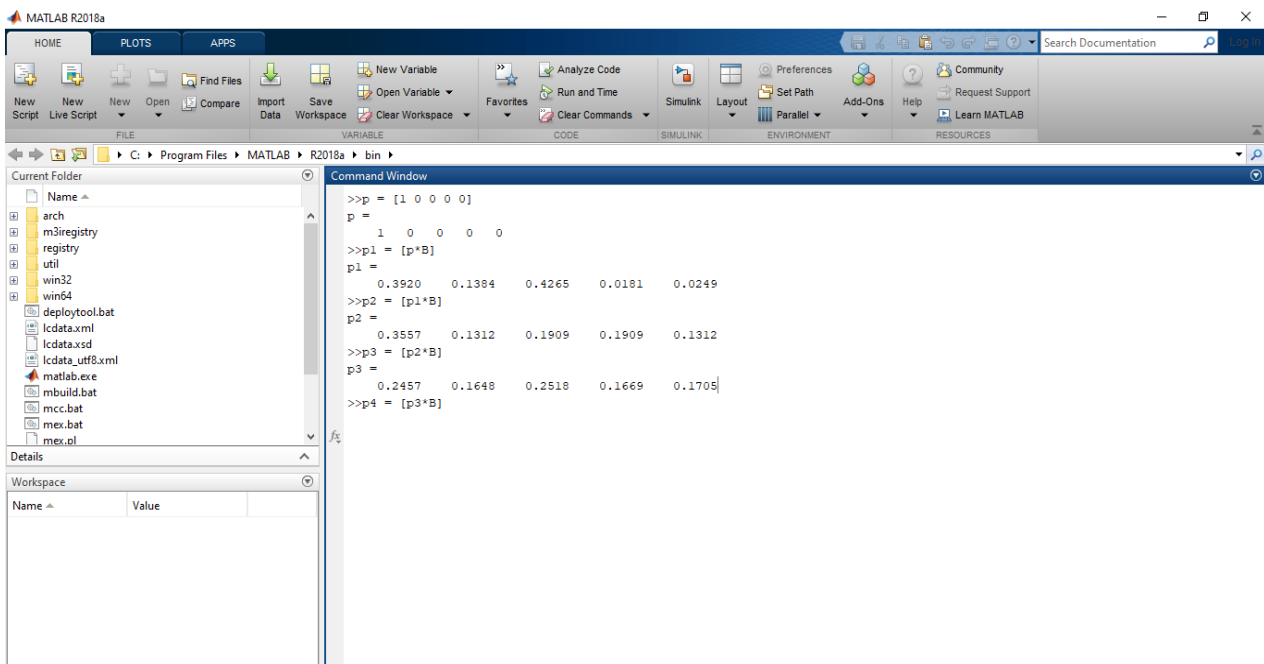

Fig. 2. Visualization of the forecasting fragment of the bioaccumulation metal coefficient states in the Matlab software environment.

And so we will carry out modeling to level the probable state of the ecological system, i. e. the optimal metal ratio in the reservoir. The simulation results are presented in table 6.

Table 6. The results of the metal bioaccumulation predicting are implemented in Matlab.

	P_1	P_2	P_3	P_4	P_5
K = 1	0.3920	0.1384	0.4265	0.0181	0.0249
K = 2	0.3557	0.1312	0.1909	0.1909	0.1312
K = 3	0.2457	0.1648	0.2518	0.1669	0.1705
K = 4	0.2338	0.1798	0.2031	0.2031	0.1798
K = 5	0.2113	0.1883	0.2125	0.1931	0.1943
K = 6	0.2079	0.1944	0.2014	0.2014	0.1944
K = 7	0.2028	0.1965	0.2030	0.1983	0.1987
K = 8	0.2018	0.1984	0.2003	0.2003	0.1984
K = 9	0.2006	0.1989	0.2006	0.1994	0.1995
K = 10	0.2003	0.1994	0.1999	0.1999	0.1994
K = 11	0.2000	0.1995	0.2000	0.1997	0.1997
K = 12	0.1999	0.1997	0.1998	0.1998	0.1997
K = 13	0.1998	0.1997	0.1998	0.1997	0.1997
K = 14	0.1998	0.1997	0.1997	0.1997	0.1997
K = 15	**0.1997**	**0.1997**	**0.1997**	**0.1997**	**0.1997**
K = 16	0.1997	0.1997	0.1997	0.1997	0.1997

The results of the simulation implemented in the Matlab software are presented in Fig. 3.
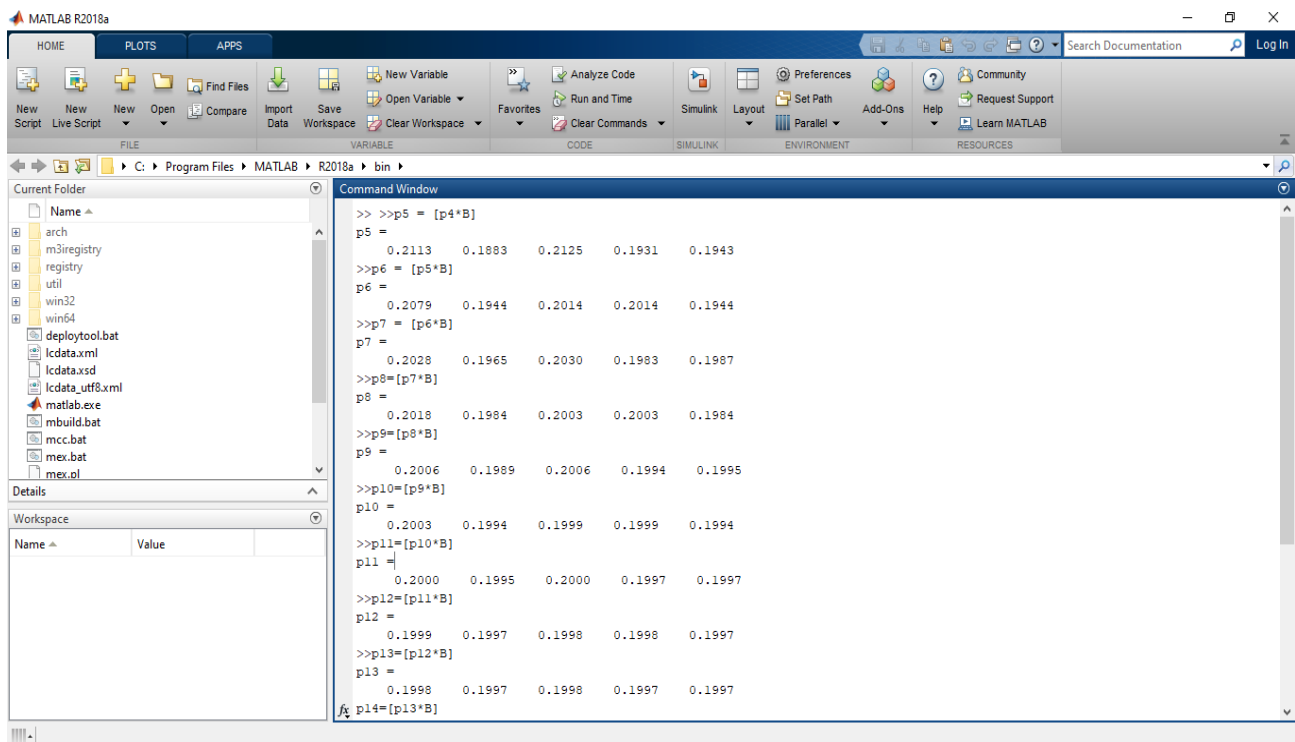

Fig. 3. Visualization of metal bioaccumulation coefficient forecasting in the Matlab software

We compare the results of forecasting the probable state of metal concentration in the reservoir for the periods of spring / above Ternopil and summer / above Ternopil, which are presented in the tables 5 and 6. The analyzing samples for spring modeling results indicate that after 9 seasons in the studied reservoir Zn concentration will more likely to be 0.2 and Cu concentration will be approximately at the same level, and metals such as Pb and Cd will approximately equally amount to 0.19. At the same modelling step for the summer period, the probable state of metal bioaccumulation is as follows: Zn – 0.2006, Mn – 0.1989, Cu – 0.2006, Pb – 0.1994, Cd – 0.1995. Thus, the reservoir will contain the most metals such as

467

Zn, Cu with a probability of 0.2206, a slightly lower Mn concentration, then Cd with a probability of bioaccumulation of 0.1995 and Pb – 0.1994.

The modelling results of probable state of metal bioaccumulation in the spring show that in the 10th season of water sampling, the same trend in the eleventh and twelfth seasons, the highest metal concentration in the reservoir will be Zn, and the lowest – Mn. During the summer, the situation with the probable state of metals at 10 and 11 steps of the simulation shows the highest bioaccumulation of metals such as Zn and Cu with coefficients 0.2003 and 0.1999 respectively, lower Mn concentration (0.1994) and higher Pb concentration (0.1999), and Cd at levels of Mn (0.1994). Comparing the results for spring and summer, it can be stated that the probability of optimal value of metal bioaccumulation in spring will be reached at the step 14, and in summer at the step 15 of the study, taking to account that the heavy metal ion accumulation by molluscs is an active and regulated process.

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).

Evidence that the Seret River is under significant anthropogenic influence is the increase in the amount of organic matter, ammonium cations, nitrite ions, chloride ions, phosphate ions and a decrease in oxygen concentration below the city of Ternopil, especially in the summer season.

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 economic-mathematical modelling tools and statistical methods based on correlation-regression analysis using modern information systems of the Matlab type 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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