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METHODS OF SLANA RIVER RESTORATION TO IMPROVE THE STATE OF ECOSYSTEM

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Abstract. The article presents the results of study on the ecological state of Slana River (Slovakia) and an assessment of catastrophic pollution due to the mine water leakage from the Siderit iron ore mine (village of Nižná Slana). The geological structure of the siderite deposit is described, the organization of geochemical data monitoring is analyzed using trend analysis and a correlation matrix for ecological and hydrochemical tasks. The study has confirmed the increased content of Fe, Ni, Mn, sulfates and As (components of the ore formation). Spatial assessment of pollution was carried out using mathematical modeling and the Google Earth platform. It was identified that in the zone of mine water leakage, there is an increase in temperature, a low level of dissolved oxygen, a reduced pH and high concentrations of sulfates, Mg, Fe, As, Co, Zn. Analysis of spatial changes showed nonlinear (parabolic) dynamics of pollutant distribution. Correlation analysis revealed a strong positive relationship between pH and dissolved oxygen (90 % probability), nitrates, sulfates, nitrogen (70–85 %), Fe–sulfates, sulfates–nitrates, Mg–COD. Negative correlation (70–80 %) is characteristic of Mg–nitrates, nitrates–dissolved solids (TDS), Ca–TDS. Environmental harm of metals is exacerbated by hardness, salinity and organic matter in water. Toxic metals (Zn, Pb, Cu, Cd) form insoluble sulfides, carbonates, precipitate (oxides/hydroxides) or co-precipitate with Fe, Mn, Al, with different redistribution rates. A combination of methods is recommended for the purification of Slana River: mechanical, physicochemical and biological with algolization of strain Chlorella vulgaris Polikarp. Optimal conditions for the development of Chlorella microalgae have been determined.

Keywords: Slana River, pollution, microalgae, Chlorella vulgaris Polikarp.

1. Introduction

Water bodies in urbanized areas are always in great danger. This is due to various types of pollution entering directly into the watercourse and reservoirs. This is especially true for surface watercourses located in the area of industrial production facilities (mines) and those under the influence of emergency discharge of mine water, which leads to an ecological disaster. In such watercourses, the life conditions of the river and coastal zone of the ecosystem, the temperature and features of the hydrochemical regimes are violated, organic pollution increases, heavy metals are accumulated, and the indicators of the ecological quality of water in the river change (Hrubinko, et al., 2023).

A similar situation regarding the catastrophic consequences of changes in the surface water quality has developed in the Slana River (Slovakia) in the south of

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the Košice Region. Due to the leakage of mine water from the iron ore mine in, the area of the former Siderit mining enterprise (iron ore mine in the village of Nyzhnya Slana (Fig. 1), highly mineralized wastewater was entering the river since February 2022, which has led to a significant deterioration of the ecosystem (Seman et al., 2024). The main threat to nature is the high content of iron, which colors the water in a characteristic red color (Fig. 1) and settles in the form of ocher, which is especially dangerous for fish – iron particles clog their gills, causing suffocation. In addition to iron, water tests revealed an excess of limits for manganese, sulfates, and arsenic (Seman et al., 2024). An additional complication is the increased water temperature, which is associated with oxidative processes in the mine and may negatively affect the biodiversity of the region in the long term. Fishing is temporarily prohibited in Slana River. The tests showed that water contains an elevated concentration of arsenic.

Fig. 1. Visualization of the pollution in Slana River near the city of Kosice (imeteo.sk)

The fishing ban applies to the section of the river from the outlet of the mine waters from the iron ore mine in the village of Nižná-Slána to the border with Hungary. In this section, the river flows through the towns of Rožňava and Tortalá, as well as the villages of Plešivec and Lenártovce. In early June 2024, the Slovak government allocated 1.5 million euros to solve the problem of Slána river pollution. The first cleaning began in the second half of July. After receiving the results of the tests, the authorities declared a state of emergency in the districts of Rožňava, Revuca and Rimavská-Sobota, through which the river flows (TASR Press agency, 2025). The Hungarian side also calls for a solution to the problem.

In order to solve the problem, the first underground works began in the second half of 2024. Mining rescuers began redirecting the flow and separating clean and contaminated water. At the end of the year, additional measures were taken to stabilize the volume of mine effluent discharge. As part of further measures, it is planned to install channels and pipelines, and build two tanks for emergency water discharge. Thus, the pollution of Slana River remains a serious environmental problem requiring an integrated approach to solve it. The distance from the source of pollution to contaminated areas has already reached more than 50 km.

In such cases, the problem of eliminating the consequences of an emergency situation associated with hazardous chemicals at the bottom of the reservoir in the area of the water intake is particularly relevant. Traditionally, physicochemical and mechanical methods are used to clean contaminated water, and overcome biological barriers. Usually, hydromechanization is used for mechanical removal of sludge and soil, with subsequent disposal, but this is a quite long and labor-demanding process.

However, these methods do not allow to sufficiently clean water from organic and inorganic pollutants entering and accumulating in surface water bodies. This leads to significant costs demand for special equipment and chemicals. Recently, under these circumstances, in many countries, including Ukraine, traditional methods of wastewater treatment and disinfection have been abandoned due to their unreliability, complexity, high cost and energy consumption. Instead of traditional treatment, methods based on biotechnological approaches, in particular, using microalgae, and new devices and equipment for their cultivation, are widely applied.

Therefore, there is an urgent need to study the ecological state of water in Slana River (analysis of monitoring data) and develop environmental protection measures to improve water quality by developing and implementing innovative technologies for the use and cultivation of microalgae, in particular the genus Chlorella strain Polikarp, which is capable to actively assimilate pollutants such as heavy metals, nitrates and phosphates, as well as saturate water with oxygen.

Discharges from metal ore mines have led to serious degradation of many rivers around the world (Allert et al., 2012; Agbam et al., 2025). Toxic metals can be extremely persistent in the environment. They can persist in floodplain sediments for decades and even millennia. According to (Byrne et al., 2012), there are metals (Fe, Mn, Pb, Al) that are almost completely bound (accumulated) with sediment due to their chemical properties. Sediment contamination in a stream generally decreases downstream from the source of contamination. The rate varies depending the ecosystem, and is negatively exponential in many cases. This pattern is functionally related to the hydraulic sorting of sediment by density and ore particle size (Jarosz-Krzemińska et al., 2015). However, according to (Jin et al., 2020), toxic metals can be attenuated downstream from the source by pH buffering, acid neutralization, precipitation and adsorption reactions. As pH increases, aqueous forms of metals tend to precipitate as carbonates, oxides, hydroxides, phosphates, silicates, or hydroxysulfates. Metal adsorption generally increases at higher pH, so significant changes in dissolved metal concentrations can occur with small changes in pH. High salinity, hardness, and organic matter are known to increase metal attenuation by providing binding sites for metal sorption. Under constant environmental conditions, the geochemical phases of sediments are stable, the chemical attenuation of metals will occur at a regular rate, and thus the metals will remain immobile in riverbed sediments (Ji et al., 2014). However, sediments are not a permanent sink for metals and they can be released into the water when the appropriate conditions for dissolution occur. Therefore, the risk of pollution posed by toxic metals stored in aquatic sediments exists as a constant long-term threat.

Typically, river cleanup after a mine water spill includes: creating physical barriers (dams to prevent the substance from flowing into water bodies, using barrier booms or construction of filter screens, container treatment facilities); diverting water away from the contaminated area to minimize contact with pollutants; using sorbents (e.g. sand, clay, peat, special industrial sorbents) around the spill site to absorb the liquid; mechanical treatment (sedimentation, filtration) to remove suspended solids; chemical treatment to oxidize and precipitate dissolved compounds, especially iron; biological methods. For effective treatment, iron oxidation methods are used, especially in cases where mine water contains dissolved divalent iron (Fe^{+2}), which is oxidized to trivalent (Fe^{+3}), forming an insoluble precipitate (rust) or sediment removal: insoluble iron compounds (Fe_2O_3) are removed by settling or filtration. For forced sedimentation of small particles, chemical reagents (flocculants) can be used.

However, modern trends in biotechnology in the form of the presence of a biological reclamation system require new approaches to clean river water from heavy metals. Bioadsorption occurs through the use of Chlorella, which is able to accumulate heavy metals, as well as actively absorb harmful substances due to cell walls. The latter have a cellulose structure and are able to bind and remove heavy metals from water (Sharylo et al., 2020; Ulytsky et al., 2023).

Perhaps, the key to a successful solution to overcome the environmental disaster in Slana River is the use of algae. This will reduce the threats and harm to the environment associated with polluted water from the Lower Slana mine after urgent measures on mechanical treatment and separating the source of clean water from polluted water or after reducing the sulfates and the total acidity of mine water by neutralizing substances and cleaning the freely flowing mine water from excessive iron, arsenic, nickel and other toxic elements.

To date, very few studies have been devoted to a detailed study of metal flows during emergency releases of mine water into water bodies and the hydrochemical variability of pollutants in time and space. Therefore, there is a need to study the ecological state of the water in the river after the accident: a detailed analysis of monitoring data and assessment of river hydrochemistry are required in order to quantify metal fluxes so that ecologists can develop environmental protection measures to improve water quality in Slana River, identify priority areas for restoration, assess the possibility of microalgae use to restore water quality. Therefore, there is a need to fill gaps in knowledge about the degradation and restoration of aquatic ecosystems.

The purpose of this work is to study the ecological state of Slana River (analysis of monitoring data in time and space) and develop environmental protection measures to improve water quality through the implementation of innovative technologies for the use and cultivation of microalgae, in particular the genus strain Chlorella Polikarp, which is capable to actively assimilate pollutants such as heavy metals, nitrates and phosphates, and saturate water with oxygen.

2. Experimental part

Spiš-Gemer ore mountains are considered the most important deposit in Slovakia. The modern base of siderite ores is represented in the area of the villages of Nižná Slána and Kobelyarovo. Today, two similar ore bodies are exploited. Mano Gabriela and Kobelyarovo deposits, which consist of metasomatic siderite with minor admixtures of ankerite, both have a variable lenticular shape. The bulk of the iron ore has an indirect thickness of 250 m, while the actual thickness of the seams is about 30 meters. Iron ore is mined underground. The only operating deep siderite mine in the world in Nižná Slána annually extracts 970 thousand tons of raw iron ore, from which 400 thousand tons of pellets are produced.

Deposits and occurrences of stratiform metasomatic siderite and ankerite occur in the Lower and Upper Paleozoic of the Hemerican Shield. In the Upper Paleozoic sediments, carbonates occur in the upper part of the black phyllites (Betli Formation), namely in the Goletka Formation, which contains black metapelites with a lithological and upper carbonate horizon.

Fig. 2. Fragment of a map with reference points (P) for monitoring with detailed results of spatial analysis of changes in geochemical indicators of water in Slana River on March 17, 2022

The main part of carbonate manifestations is represented by bodies of ankerites, crystalline marbles and dolomites. Only some of them are siderites, which were mined in Zheleznik, Rakosy, Hradok, Gampel, Ignac, or some of them are mined now in Nizhnya Slana – Mano, Kobelyarovo. The territory of the deposit belongs to the ankerite zone of Gankova – Volovets – Golets. Several types of tectonic structures are distinguished in the deposit. The greatest influence on the deposit had the crushing of the entire layer and the formation of shallow tectonic scales. The main tectonic structure of the ore field is an asymmetric anticline with a lowered northern flank. The Mano deposit is located in the zone of sedimentary rocks between volcanic rocks and has an arc-shaped occurrence. The deposit has a strike length of 2.3 km, after a dip of 1.2 km, with a total dip of 30° to the south and southeast. The thickness of the formation is up to 450 m. It contains a carbonate-lydite horizon with carbonates metasomatically altered to ankerite and siderite. Siderite is common in the central part of the deposit, with a strike length of about 800 m and a dip length of 350 m. In the deposit belt, siderite consists of several positions separated by different layers (black phyllites, limestones, ankerites). The actual thickness of individual layers is variable, in exceptional cases reaching 50 m. The deposit mainly consists of metasomatic ankerite and siderite, which contain the bulk of iron, while other minerals are insignificant in terms of deposition. Fine-grained siderite has a high iron content, as well as an increased Mn content, and the Mg content decreases with increasing Fe and Mn content. That is, iron and manganese are useful elements in the deposit. The average content of Fe and Mn in the ore is 33.5 % and 2.18 %, respectively. Unwanted impurities in the deposit include mainly arsenic, sulfur, lead and zinc, which occur in the form of oxides, sulfides, sulfates and sulfosalts. Among these impurities in the mined ore, much attention is paid to arsenic mainly bounded in arsenopyrite. It is developed in separate areas of contact of the siderite position with the overlying black phyllites and liliths. The average As content in the mined ore ranges from 0.01 to 0.1 % (Kiefer et al., 2020).

All the listed parameters indicate that upstream of Slana River (relative to the town of Nyzhnia Slana), there are manifestations of siderite and ankerite, which affect the background concentrations of chemical elements and compounds in rocks and soils that can enter river water, influencing its chemical composition. The impact of these background concentrations depends on the type of deposit and its geological structure: they can either slightly enrich the water or lead to a significant excess of the maximum permissible concentration (MPC) of certain substances. The presence of additional pollution due to the emissions of the existing iron ore mining and processing plant in Nyzhnia Slana also poses a constant danger of toxic elements transportation and transformation. Soil research on the territory of this plant (Fazekašová et al., 2020) showed the content of Hg, Cd, Cr, Cu, As, Fe, Mn and Mg exceeds the toxicity level. As, Fe, Mn and Mg are the most important pollutants: maximum values exceed the average Fe content by up to 6.7 times, Mg content is 26–53 times higher than the MPC. Studies on soil contamination by As deserve special attention associated not only with anthropogenic impact, but also with geochemical impact, which is confirmed by research. The presence of tectonic disturbances, fracture zones also add certain changes to the chemical composition of water bodies. They facilitate substances leaching and affect changes in the groundwater and surface water quality (Levoniuk et al., 2019). That is, the chemical composition of water samples at point S006500O Slana – Nyzhnoslanska Banya, 67.75 km (bridge through the plant) can be assumed as background.

To understand the full impact, it is necessary to conduct comprehensive research on the chemical composition of the deposit, soils and water in the river, as well as take into account modern anthropogenic factors. To achieve the goal, the following research methods were used: correlation analysis of geochemical data on river water monitoring, graphical analysis of temporal information of geochemical indicators, analysis of spatial interpolation of geochemical indicators of Slana River, calculation of the optical density coefficient, which reflects the concentration of algae in water, biological methods of water cleaning from heavy metals, a method of cultivating a new strain of green algae strain Chlorella Polikarp and its use for biological rehabilitation of surface waters.

3. Results and Discussion

Monitoring of chemical parameters of Slana River was first carried out at 3 observation points (P1, P2, P3) (Fig. 2) on 03.17.22 (Table 1).

Table 1

Characteristics of mine water samples

Chemical indicator	Unit	Water sampling points				K=Ci/Cn	
		S006500O Slana – Nizhne slanska Banya, km 67.75, C1	S0065PVA Nižná Slaná mine, mine water outlet, C2	S007000O Slana – Lower Slana. km, 66.0, C3	MPC. (Government Decree of the Slovak Republic 269/2010, item 1. 5), Cn	K_2	K_3
Water temperature	°C	5.7	30.5	5.7	<26		
Dissolved oxygen	mg/dm^3	13.80	3.08	11.70	more than 5		
BOD	mg/dm^3	1.35	11.30	3.60	7	1.7	0.5
COD	mg/dm^3	4.56	1220	11.80	35	34.9	0.34
pH		8.82	5.81	726	6–8.5		
TDS105	mg/dm^3	170	80030	1690	900	88.9	1.88
TDS550	mg/dm^3	128	42980	1250	640	67.16	1.95
EC25	mS/m	28.20		120	110		1.09
Fe	mg/dm^3	0.45	5810	82.10	2	2905	41.1
Mn	mg/dm^3	0.072	584	9.81	0.3	1946	32.7
NO_3	mg/dm^3	1.56	39.10	2.49	5.0	7.8	0.5
Total phosphorus	mg/dm^3	0.034	3.18	0.024	0.4	7.9	0.1
Total nitrogen	mg/dm^3	1.42	7.49	1.23	9	0.8	0.1
Sulfates	mg/dm^3	39.20	35500	1090	250	142	4.4
Mg	mg/dm^3	2.27	1830	578	100	18.3	5.78
Hg. dissolved	mg/dm^3	0.70	6800	262	200	34	1.5
Cd. dissolved	mg/dm^3	< 0.024		0.028	1.5		0.02
Pb. dissolved	mg/dm^3	2.93	12.70	2.24	20	0.6	0.1
As. dissolved	mg/dm^3	5.51	14000	224	20	700	11.2
Cu. dissolved	mg/dm^3	10.0	38.70	2.78	20	1.9	0.14
Cr. dissolved	mg/dm^3	0.67		2.55	50		0.05
Ni. dissolved	mg/dm^3	1.87	21500	357	20	1075	17.9
Zn. dissolved	mg/dm^3	40.60	2830	70.5	100	28.3	0.7

Note: * – normative values are given in accordance with the Decree of the Government of the Slovak Republic: No. 269/2010, Annex 1, 5. Coll. of Laws, which establishes requirements for achieving good water status. Pollution coefficients (K2, K3) exceeding the MPC are highlighted in red. C1, C2, C3 – concentration of the chemical indicator at the monitoring point, ** date of water sampling 17.03.2022.

Water sampling sites along Slana River:

1. P1. S006500O Slana – Nizhnyoslanska mine, r. km 67.4 (bridge under the former plant);
2. P2. S0065PVA Rudne Bane, s.l. Nizhnya Slana, mine water outlet, siderite ore deposit (source of pollution);
3. P3. S007000O Slana Nizhnya Slana, r. km 66 (bridge);

4. P4. S053000D Slana Choltovo, r. km 28.2;

5. P5. S131000D Slana Lenartovce, r. km 3.3 (above the mouth of the Rymava River).

The distances between the observation points are from 700 to 1500 m. The coefficients of MPC exceeding (K2, K3) indicate that the mine water leaked almost a month after the accident did not affect the geochemical indicators of water in Slana River upstream. Analysis of spatial changes in geochemical indicators showed that almost all of them had maximum values (except for the hydrogen) in the area of mine water leakage, which greatly affected the water temperature in Slana River. It is clear that it is impossible to find out the spatial distribution patterns across three observation points, but it was important to determine the general trends in pollution and catastrophic consequences of the accident. According to observations on 03.17.2022, the excess of the elements content compared to the MPC occurred at monitoring points P2 and P3: Fe (P2 – 2905 times, P3 – 41 times); Mn (P2 – 1946 times, P3 – 32.7 times); Mg (P2 – 18.3 times, P3 – 5.78 times); Hg (P2 – 34 times, P3 – 1.73 times); As (P2 – 700 times, P3 – 11.72 times); Ni (P2 – 1075 times, P3 – 17.9 times); Zn (P2 – 28.3 times, P3 – 0.7 times); sulfates (P2 – 142 times, P3 – 4.4 times). Very high water temperature was registered. pH in the leak zone had a low value (5.81), i.e. an acidic environment was formed.

Analysis of the results obtained indicates that the influx of large volumes of silted material into the river ecosystem can change local mass transport and sediment deposition, and have an impact on various chemical processes in both water and soil of the river bed.

To conduct a temporal analysis of geochemical data, it was decided to expand the range and profile of monitoring observations (Table 2). The study showed that at the mine water leakage site, an increased temperature, a low dissolved oxygen, a decreased pH, and an increased concentrations of sulfates, magnesium, iron, arsenic, cobalt, and zinc were observed for almost four months after the accident.

Table 2

Comparison of monitoring results for the period 03.2022 – 06.2022: S0065PVA Rudné bane, mine water discharge– source of pollution

Chemical indicator	Unit of measurement	17.03. 2022	30.03. 2022	04.05. 2022	01.06 2022	14.06. 2022	28.06. 2022	Government Decree of the Slovak Republic 269/2010, item 1, 5)
Visual color		brown-red	brown-red.	brown-yellow	brown-red.	brown-red.	yellow-brown	
Water temperature	°C	30.5	31.7	32.6	32.6	17.8	14.3	more than 5
Dissolved oxygen	mg/dm^3	3.08	2.54	3.63	3.67	7.47	8.97	7
BOD	mg/dm^3	11.3	11.9	14.3	15.2	11.3	11.4	35
COD	mg/dm^3	1220	1320	1220	1238	493.0	178	-
pH		5.81	5.67	5.53	5.6	5.53	6.74	
Fe	mg/dm^3	5810	1230	623	709	246	81.4	2
Mn	mg/dm^3	584	5.87	1.22	1.22	1.22	1.22	0.3
NO_3	mg/dm^3	39.1	16.6	0.22	0.14	2.47	0.03	5.0
Total phosphorus	mg/dm^3	3.18	5.37	5.93	6.09	2.13	1.43	0.4
Sulfates	mg/dm^3	35500	41200	2850	3250	2890	2520	250
Mg	mg/dm^3	1830	1830	4690	4810	6640	432	200
Hg, dissolved	mg/dm^3	6800	0.05	0.05	0.05	0.05		1.5
Cd, dissolved	mg/dm^3		0.49	1.19	0.99	0.35	0.049	20
Pb, dissolved	mg/dm^3	12.7	0.30	1.0	1.0	2.8	0.3	20
As, dissolved	mg/dm^3	14000	7140	6710	10744	8800	1180	20
Cu, dissolved	mg/dm^3	38.7	0.50	1.0	1.0	2.9	0.50	50
Cr, dissolved	mg/dm^3		0.50	2.0	2.0	2.9	0.50	20
Ni, dissolved	mg/dm^3	21500	21500	25436	22991	9684	3110	100
Zn, dissolved	mg/dm^3	2830	20091	1734	1220	1340	397	500
Sb, dissolved	mg/dm^3	-	-	438	31.9	21.6	5	50
Co, dissolved	mg/dm^3			4500	4044	1580	-	1.5

Note: * DO – dissolved oxygen; COD – Chemical oxygen demand; BOD – Biochemical oxygen demand; EC_{25} – Electrical conductivity at 25 °C; TDS_{105} – dissolved solids dried at 105 °C.

However, analysis of spatial changes in concentrations (CC) of geochemical parameters (Figs. 3, 4) showed that the CC process is not linear over time. It is described by a second-order polynomial (quadratic trinomial) and most confidently shows a parabolic relationship between variables, which indicates the complexity of the process. The second-order polynomial is part of the Taylor expansion. It can be used to approximate more complex functions, i.e. to show that initially concentrations increase with temperature increasing, reach a maximum, and then begin to decrease as the temperature becomes lower. For pH, this process has an inverse relationship. The higher the value of the coefficient of determination, which shows how much of the variation in the dependent variable is explained by the independent variables in the statistical model (R^2), the better the model explains the result. In this case study, we have quite large R^2 indicators (0.883, 0.7855, 0.7623, 0.9266, etc.).

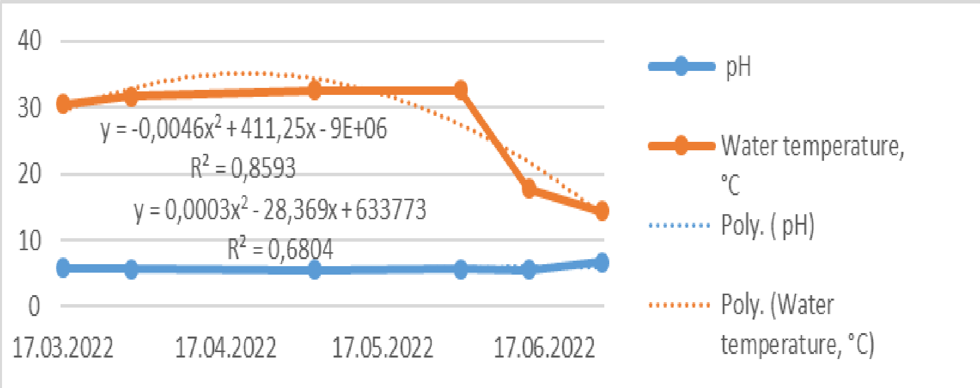


Fig. 3. The result of time analysis of changes in geochemical indicators of water in Slana River at the mine water outlet point in the period from March 22 to June 22 using trend analysis elements

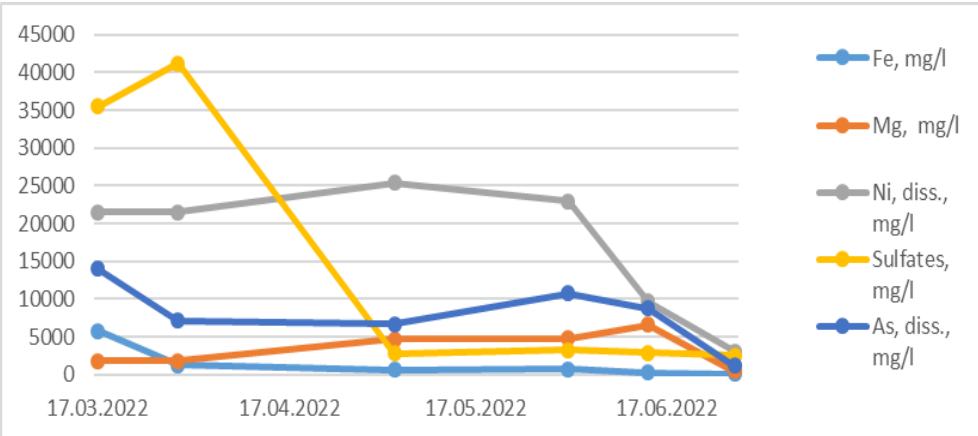


Fig. 4. The result of time analysis of changes in geochemical indicators of water in Slana River at the mine water outlet point in the period from March 22 to June 22

The ability to find out the “relationships” of individual measurement indicators as interconnected (or vice versa) elements is provided by the mathematical calculation of the correlation matrix, made in the Data Analysis program (Table 3).

Based on the results obtained, it can be stated that during the monitoring period, a very high correlation index has a relationship between pH and dissolved oxygen. That is, an increase in one indicator with a probability of 90 % affects an increase in the other. Practically the same relationship exists between the content of nitrates, sulfates, nitrogen and dissolved oxygen (at 70–85 %). A high correlation relationship is also registered for iron-sulfates, sulfates-nitrates and magnesium-COD. A negative correlation (70–80 %) indicates an opposite correlation relationship with a high probability between the content of magnesium and nitrates, nitrates and dissolved solids, calcium and dissolved solids. Other geochemical indicators have a lower correlation (slightly more than 60 %): BOD and total nitrogen, pH, ammonia and dissolved oxygen, etc. There are measurement indicators, the content of which does not affect the content of others in any way, their correlation coefficient is very small. At the same time, the environmental damage of the metal mixture is enhanced by water quality (hardness, salinity and organic matter content). These parameters can increase or decrease the toxicity of metals. As a rule, a decrease in pH leads to an increase in the amount of toxic free metal ions due to changes in the metal composition. However, at low pH, metals tend to be desorbed due to competition with hydrogen ions. All of the above changes primarily affect the river biota. Analysis of the results obtained allowed us to establish that toxic metals (e.g., zinc, lead, copper, cadmium) can form insoluble sulfides and metal carbonates and can be removed either by direct precipitation in the form of oxides and hydroxides or carbonates, or by co-precipitation with hydroxides of iron, manganese and aluminum. However, the removal rate of toxic metals in these systems is different. Therefore, river floodplain or bottom silt deposits can be a significant secondary diffuse source of pollution. The river will continue to pose a serious threat to environmental safety if relevant measures are not taken.

Table 3

Result of mathematical calculation of the correlation matrix

	DO	BOD	COD	pH	TDS_{105}	TDS_{550}	EC_{25}	Fe	Mn	NH_4	NO_3^-	P_{tot}	N_{tot}	S	Ca	Mg
DO	1															
BOD	-0.268	1														
COD	-0.485	0.170	1													
pH	0.900	0.011	-0.278	1												
TDS_{105}	0.429	0.141	-0.209	0.319	1											
TDS_{550}	-0.536	0.796	0.420	-0.279	0.178	1										
EC_{25}	0.116	0.055	0.139	0.071	0.735	0.045	1									
Fe	0.576	0.129	0.468	0.694	0.108	-0.357	0.207	1								
Mn	0.218	-0.084	0.204	0.382	0.169	-0.214	0.634	0.619	1							
NH_4	-0.642	0.235	0.052	-0.611	0.260	0.562	0.362	-0.295	0.023	1						
NO_3^-	0.856	-0.532	-0.623	0.727	0.039	-0.518	-0.105	0.652	0.255	-0.631	1					
P_{tot}	-0.173	0.204	0.003	-0.357	0.214	-0.065	0.456	-0.032	-0.047	0.060	-0.260	1				
N_{tot}	0.723	-0.614	-0.609	0.480	0.482	-0.510	0.094	0.169	0.003	-0.156	0.703	-0.353	1			
SO_4	0.806	-0.252	-0.447	0.708	0.424	-0.637	0.489	0.793	0.604	-0.414	0.777	0.177	0.502	1		
Ca	-0.467	-0.296	0.361	-0.548	-0.778	-0.165	-0.601	-0.601	-0.501	-0.276	-0.237	0.065	-0.390	0.576	1	
Mg	-0.678	0.118	0.833	-0.49	0.005	0.460	0.455	-0.473	0.319	0.536	-0.750	0.159	-0.527	-0.422	0.136	1

Note: * green color – negative correlation; orange color – positive correlation.

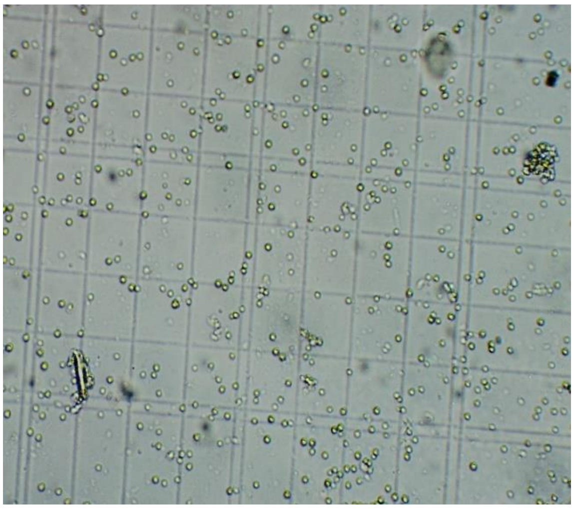
Technologies for treating river water in case of local pollution can be divided into the following categories: mechanical, chemical and biological. However, the implementation of treatment systems should include measuring seasonal variations and taking into account the impact of episodic events of pollutant washout (for example, associated with water flows during floods). First of all, it is necessary to collect and direct contaminated effluents to treatment areas. In general, to clean Slana River, it is necessary to use a combination of mechanical (grids, filters, settling, pumping sediment from the river with a submersible pump (sludge pump) able to work with abrasive particles and sticky mass contained in the sludge, physicochemical (coagulation, chemical reagents, sorption) and biological methods, in particular algolization (saturation of natural water bodies with microscopic algae, in particular chlorella, to improve water quality and eliminate excessive pollution).

The practical part of the experiment on the introduction of Chlorella for algolization of Slana River (Slovakia) was carried out in the water sampled after the mine water leakage site. The experiment can be considered from various aspects of the microorganisms functioning in water contaminated by heavy metals (HM):

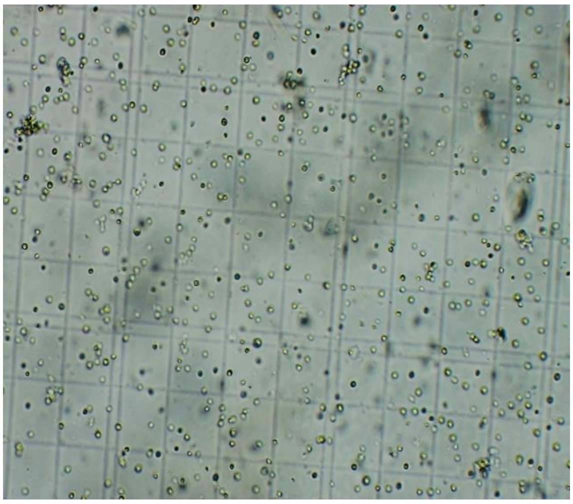
– as the probability of use as test organisms or indicator organisms;

– as the prospect of using individual microbial communities.

When assessing changes in the quality of Slana River waters, the optical density coefficient was used, which reflected the concentration of algae in the water (Fig. 5). The author of the study patented a method for cultivating a new strain of green algae strain Chlorella vulgaris Polikarp (Pashkevich, 2017), which he used to conduct an experiment on algolization of surface waters. The main thing in this case was the development of technologies for growing, based on the highly productive Chlorella strain, mixed strains using local microalgae cultures to create sustainable biomass producers depending on the type of water body use (Ulytsky et al., 2023).



A – microalgae population of the strain Chlorella vulgaris Polikarp



B – fragment after 3 days of growth Chlorella vulgaris Polikarp

Fig. 5. Fragments of colonization of Chlorella microalgae strain Polikarp

The strain of microalgae Chlorella vulgaris is deposited in the collection of the Institute of Botany named after M. G. Kholodny of the National Academy of Sciences of Ukraine (acronym IBASU-A), which is part of the National Herbarium of Ukraine, under the name Polikarp. The collection of microalgae cultures (IBASU- A) is considered independently as an object of national heritage. According to the results of molecular-phylogenetic study, nucleotide sequences of the 18S pPHK gene of Ch. vulgaris Polikarp were obtained, which were deposited in the GenBank database under number MW008650.1.

According to the results of using the strain Chlorella vulgaris Polikarp, it was concluded that chlorella is able to remove heavy metals from Slana River through several mechanisms (Tymurova et al., 2025):
1. Biosorption: Heavy metal ions are adsorbed on the surface of the chlorella cell walls. This is a rapid process not requiring metabolic activity of cells.
2. Bioaccumulation: Heavy metals are absorbed by chlorella cells and accumulated inside them. This process is metabolically dependent.

It is very important that microalgae can form complexes: chlorella can secrete certain substances that bind heavy metals, making them less toxic or promoting their precipitation. It is important to note that most examples of the chlorella use for industrial wastewater treatment from heavy metals are laboratory and pilot studies, since the full implementation of biotechnology at industrial scale often requires significant investments and further optimizations.

The use of Chlorella vulgaris Polikarp biomass in laboratory conditions for Slana River cleaning provided the removal efficiencies: Cu: 39–95 %, Cd: 57–96 %, Ni: 32–99 %, Pb: 48–99 %, Zn: 51–98 %. The optimal pH for heavy metals removal by chlorella is often in the range of 6–7. The optimal temperature is around 25 °C (Petruk et al., 2024). Chlorella can effectively remove metals from of low and relatively high concentrations. Studies show that both living and non-living chlorella cells are capable of heavy metal biosorption. Moreover, in some cases, dry algal biomass can absorb even more metals than living cells due to the increased surface area and accessibility of functional groups.

The conducted study demonstrate the significant potential of chlorella in solving the problem of heavy metal pollution of water bodies. However, the transition from laboratory research to full-scale industrial application requires further research, process optimization and development of economically viable technologies. However, the effect of using chlorella-based biological preparations may be slower compared to some chemical methods and mechanical methods of water treatment. The disadvantage of chlorella use is the need to utilize biomass to avoid secondary pollution.

4. Conclusions

The Slana River, a right tributary of the Tisza River, flowing in Slovakia and Hungary, has been declared an emergency area in the localities of Rožňava, Revuca and Rymavská Sobota due to the leakage of mine waters from an iron ore mine on the territory of the former Siderit mining company. Pollution by mine waters is one of the most large-scale and dangerous types of technogenic impact on the environment. The study confirmed the increased content of iron, nickel, manganese, sulfates and the presence of arsenic (components of the ore formation) in Slana River. The pollution indicators and their intensity were defined on the basis of geochemical studies using modern software products for mathematical modeling and the Google Earth satellite imagery platform. The mathematical models of pollutant distribution in time and space were created in the study. It was established that the mine water leakage site has an increase in temperature, a low dissolved oxygen, a reduced pH, and increased concentrations of sulfates, magnesium, iron, arsenic, cobalt, and zinc. This trend persisted for almost four months after the accident. Analysis of spatial correlation coefficients for geochemical indicators showed that changes over time are not linear. It is described by a second-order polynomial and shows a parabolic relationship between variables, which indicates the complexity of the pollutant distribution process. This complex function shows that initially the concentrations increase with increasing temperature, reach a maximum, and then begin to decrease when the temperature becomes lower. This process has an inverse relationship for pH. Based on the results of the correlation matrix evaluation, it can be stated that the relationship between pH and dissolved oxygen has a very high correlation index. That is, an increase in one indicator with a probability of 90 % affects the increase in the other. The same relationship (70–85 %) was found between the content of nitrates, sulfates, nitrogen and dissolved oxygen A high correlation relationship was registered for iron-sulfates, sulfates-nitrates and magnesium-COD. A negative correlation (70–80 %) was found for the content of magnesium and nitrates, nitrates and dissolved solids, calcium and dissolved solids. The environmental damage of the metals mixture in water is enhanced by water quality (hardness, salinity and content of organic substances). All of the above changes, first of all, affect the river biota. Analysis of the results showed that toxic metals (e.g., zinc, lead, copper, cadmium) can form insoluble metal sulfides and carbonates and can be remobilized either by direct precipitation as oxides and hydroxides or carbonates, or by co-precipitation with iron, manganese, and aluminum hydroxides. However, the removal rates of toxic metals in these systems vary.

For the purification of Slana River, the following recommendations are suggested: use a combination of mechanical (grids, filters, settling, pumping out sediment from the river with a submersible pump (sludge pump), physicochemical (coagulation, chemical reagents, sorption) and biological methods, in particular algolization with Chlorella vulgaris Polikarp strain. The use of Chlorella vulgaris Polikarp biomass in laboratory conditions for the purification of water from Slana River, achieved the removal efficiency: Cu: 39–95 %, Cd: 57–6 %, Ni: 32–99 %, Pb: 48–99 %, Zn: 51–98 %. The conditions for using microalgae were determined: the optimal pH for the removal of heavy metals by chlorella is in the range of 6–7; the optimal temperature is about 25 °C.

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