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Impact of the geological structure on the development of anthropogenic-karstic reservoirs diverse hydrologically and hydrochemically

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Abstract: The deep exploitation of mineral deposits is carried out in many areas around the world. However, one of its negative consequences is surface deformations. These may be discontinuous deformations (sinkholes) or continuous deformations (subsidence basins).

Under specific hydrogeological conditions, these forms are inundated, and thus anthropogenic reservoirs are formed. In some post-mining areas, the number of such reservoirs is so large that they are referred to as "anthropogenic lake districts". Depending on the geological structure of the deposit and the mining technique, these reservoirs may have different morphometric parameters. Moreover, they may show various hydrological conditions and physicochemical properties of their waters.

The article describes a unique group of anthropogenic water reservoirs created due to the flooding of deep salt mines on the Solotvyno mining field. Although small in terms of the area, it includes a group of anthropogenic water reservoirs highly diverse in terms of their genetics, hydrology and hydrochemistry. Some of them represent a unique type of meromictic reservoirs. This research shows the direction in which water conditions may change in other mining areas with significant surface deformation across the globe.

Keywords: anthropogenic-karstic reservoir, hydrochemical type, hydrochemistry, mine water, salt mining

INTRODUCTION

Anthropogenic water reservoirs are a new element of the natural environment. We can distinguish four groups: dam reservoirs (including breeding ponds (Khilchevskyi *et al.*, 2020)), reservoirs in sinkholes and subsidence basins, post-exploitation reservoirs, and industrial reservoirs. A particularly interesting group of reservoirs are those filling in sinkholes and subsidence basins. They form due to the underground exploitation of mineral deposits, which results in the development of underground voids. The morphological consequence of the collapse of an underground void is a sinkhole or subsidence basin. The development of these forms is often a long-term process and consists of a slow but systematic lowering of the area. The shapes of subsidence basins most often resemble an ellipse, while the shapes of sinkholes resemble a circle. In a specific hydrogeological situation, rainwater or groundwater accumulates in these forms and thus leads to the formation of a reservoir (Rzętała, 2008). Although these reservoirs do not have a natural origin, they undergo the same processes as natural lakes (Molenda and Kidawa, 2020).

The reservoirs that develop in rock salt mining are as specific (Lachhab *et al.*, 2022). A considerable accumulation of such reservoirs may be the effect of a water disaster and flooding of the mine (Mycielska-Dowgiałło *et al.*, 2001). Such a situation also occurred in the Solotvyno field in southwestern Ukraine. The article describes the processes that had led to the creation of reservoirs in anthropogenic-karstic sinkholes. The classification of reservoirs, both in terms of hydrology and hydrochemistry, is also presented. Particular attention is paid to recognising the processes that had led to the development of a meromictic phenomenon in the studied reservoirs.

MATERIALS AND METHODS

LOCATION OF THE RESEARCH AREA

The studied reservoirs are located in Solotvyno in Zakarpattia Oblast' (SW Ukraine, 47°57'12.6"N 23°52'03.2"E), near the border with Romania (Fig. 1). In terms of the geological structure, there is a salt dome here formed by salts of the evaporite formation. The dome reaches the surface; on the plane it has an elliptical shape. The longer axis runs close to W–E, and the shorter to N–S direction. The dome widens considerably with increasing depth. Its geological structure is complex, with the steep dip of the layers characteristic of salt domes (Dyakiv, 2012). On the dome's roof, there are loose sediments represented by sands and gravels of the meadow terrace of the Tisza River.

The reservoirs in question are located within the right-bank meadow terrace of the Tisza River at an altitude of ca. 280 m.

The average annual air temperature in the area is 8.8°C, with the lowest in January (−3.5°C) and the highest in July (18.8°C). The average annual rainfall is 744 mm, with the highest in June (101 mm) and the lowest in March (42 mm).

In the Solotvyno salt dome area, the exploitation of salt deposits was carried out by both open-pit and deep mining methods. Open-cast mining was mainly carried out in the outcrop zone of salt deposits. Even in the 1970s, it was possible to observe outcroppings of salt deposits called "salt mountains". Underground (deep) exploitation of Solotvyno salt deposits was carried out in both the chamber and chamber-pillar systems. The chamber system was used in the initial period of operation. The depth of the excavations from the ground surface reached a maximum of 300 m. At the end of the 20th century, the deposit was accessed through several shafts. As a result, a system of over 50 underground chambers was created. In 2008, vast amounts of water began to flow into the mine at 500–600 $m^3 \cdot h^{-1}$. As a result, with the inability to pump out such large amounts of water, a water disaster and flooding of the mines occurred. Currently, all the deep mines that used to operate in the area of the Solotvyno deposit are flooded.

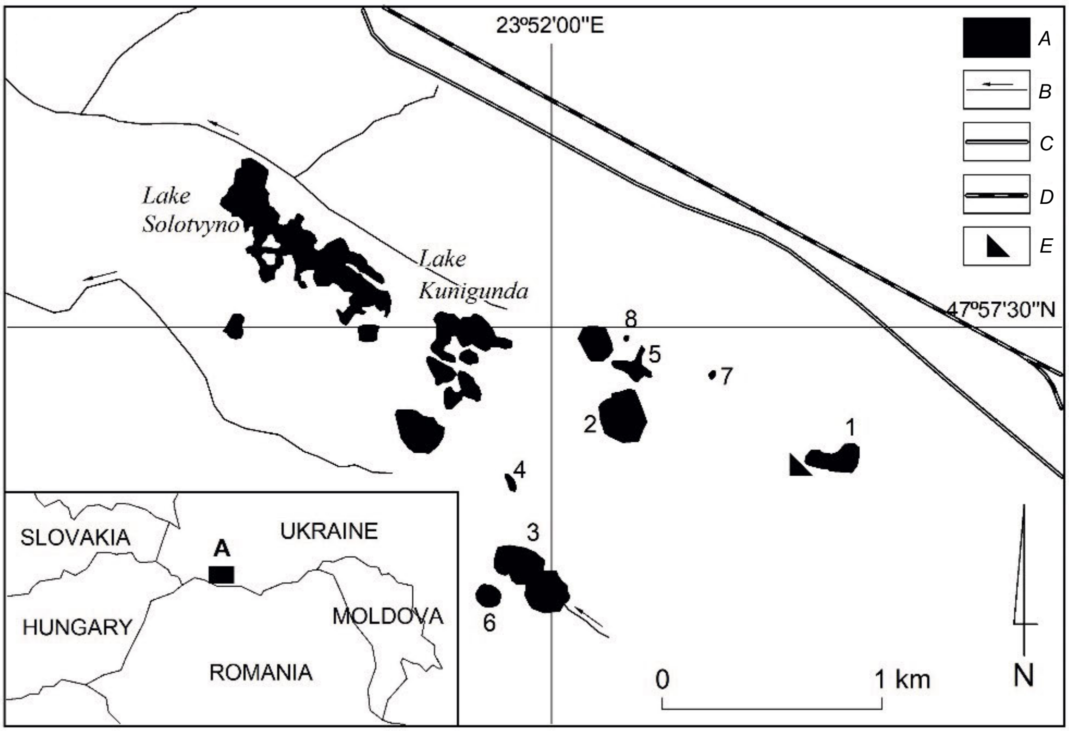

Fig. 1. Location of the research area: *1–8* = reservoirs, *A* = anthropogenic reservoirs, *B* = stream, *C* = roads, *D* = railway line, *E* = landfills municipal; source: own elaboration

METHODS

Hydrographic mapping allowing the assessment of water conditions within the Solotvyno mining field was carried out following the guidelines provided by Gutry-Korycka and Werner-Więckowska (1996). The origin and hydrological type of the reservoirs were established. Measurement profiles were located in the central (deepest) part of reservoirs No. 3 and 5.

The measuring point was reached using a pontoon. The lowering of the measuring equipment and the author's descent to the bottom of the sinkholes was carried out using mountaineering techniques (harness, rope). In the profile, the basic physicochemical parameters of water (temperature, pH, redox potential, electrical conductivity and water oxygen saturation) were measured using a multi-parameter YSI 6600 m and transparency using a Secchi disk (SD). Before every research, the probe was calibrated using standard solutions. These water parameters were determined in the lake in a water column every 1.0 m. In the remaining reservoirs (No. 1, 2, 4, 6, 7, 8), water samples were taken from the surface layer (~0.5 m) using a telescopic boom.

During the field research, water samples for chemical analyses were collected in polyethene bottles. The bottom water samples were taken using a Van Dorn bathometer. Transport of water samples to the laboratory was carried out at a temperature of +4°C. Before the analyses, the samples were filtered on a 0.45 µm filter (Millipore). The laboratory analyses included determination of the major cations and anions in the water: Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+, SO_4^{2-}, Cl^-, Br^-, NO_2^-, NO_3^-, and PO_4^{2-}. The analyses were performed on an ion chromatograph Metrohm 850 Professional IC (anion column A Suup 7-250/4.0, eluent 3.6 mM Na_2CO_3 and a cation column C4-150/4, eluent 0.7 mM dipicolinic acid and 1.7 mM HNO_3). Bicarbonates (HCO_3^-) were determined by titration with the basicity index b-r (blue-red). The hydrochemical type of waters was classified based on the Szczukariev-Pryklonsky classification (Macioszczyk and Dobrzyński, 2002).

RESULTS AND DISCUSSION

MORPHOMETRIC AND HYDROLOGICAL CHARACTERISTICS OF THE STUDIED RESERVOIRS

The inflow of groundwater to the mines and their subsequent flooding led to the activation of karst processes. As a result, clamping and destabilisation of sidewalls and ceilings within the post-mining chambers took place rapidly (Dyakiv, 2012). The effects of these processes were revealed on the ground surface in the form of continuous deformations (subsidence basins) and discontinuous deformations (sinkholes). Generally, these types of forms are referred to as **anthropogenic-karstic**. Such forms are known from other places of rock salt mining, for example, in Russia and Poland (Mycielska-Dowgiałło *et al*., 2001; Andrejchuk, 2002). The most spectacular forms are the sinkholes (Photo 1). Several dozen forms of this type have been identified in the area of the Solotvyno deposit. The most extensive forms developed when the roof of the excavation chamber located at a small depth from the ground surface collapsed.

Photo 1. "Solotvyno No. 2" reservoir in the anthropogenic sinkholes (phot.: *T. Molenda*)

Considering the classification of karst craters proposed by Ford and Williams (1989), this type can be classified as **collapsed-corrosive**. It is the genesis of reservoir No. 2 (Fig. 2). A characteristic feature of its coastline is the presence of salt rock outcrops (Photo 2). Other karst sinkholes developed in the overburden rocks (sands with gravels or clay); they represent the **subsidence** type (Fig. 3). Reservoir No. 5 is an example of this type of waterbody (Fig. 3). Notably, the development of these forms takes place directly above the excavation chambers and includes adjacent areas. It is related to salt leaching outside the excavation area. In addition to single sinkholes, there are also complex forms, and the development of larger sinkhole clusters can lead to the formation of larger forms, equivalents of an uvala (Serb.). An example of such a form is reservoir No. 3, which developed by combining two sinkholes. In the future, reservoir No. 3 is going to connect with reservoir No. 6. In the zone between the reservoirs, intensive

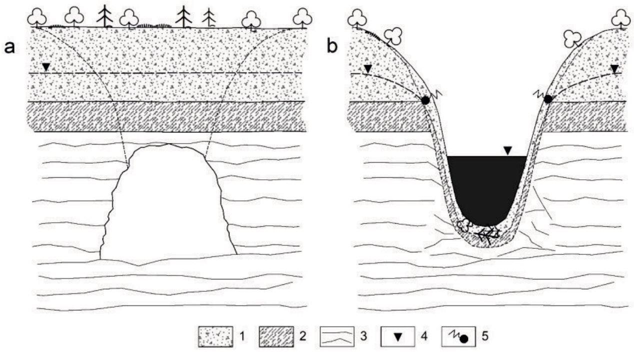

Fig. 2. Scheme of creating a water reservoir in the collapse-corrosive: *1* = sand and gravel, *2* = clay, *3* = salt, *4* = water table, *5* = source; source: own elaboration

Photo 2. Shore zone of the reservoir „Solotvyno No. 2" (phot.: *T. Molenda*)

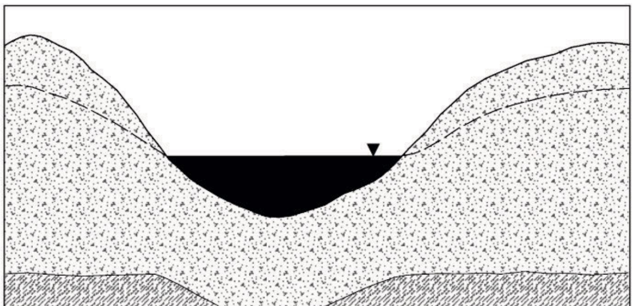

Fig. 3. Scheme of creating a water reservoir in the karst sinkholes with subsidence: *1* = sand and gravel, *2* = clay, *3* = salt; source: own elaboration

subsidence and the development of landslide fissures have been observed. Nevertheless, the vast majority of sinkholes remain dry, and only a few are submerged. Submerged forms create anthropogenic water reservoirs.

In terms of hydrology, all reservoirs in the Solotvyno area are **endorheic**. However, they differ in the water supply mechanism. The dominant role in supplying the reservoirs is groundwater draining the Quaternary aquifer (Fig. 2). The water outflow occurs most often where a layer of gravel is in contact with clays. A specific type of layered-contact outflows arises, which in some places have a concentrated form (sources). Rainwater directly falling onto the surface of the reservoir and surface runoff play a minor role. The situation is different in the case of reservoir No. 3. It developed on the axis of a small watercourse valley (Fig. 1). The catchment area (up to the inflow to the reservoir) is 0.35 km^2, and the average flow is 3 $dm^3 \cdot s^{-1}$. Most of the waters flowing in the stream are domestic and economic sewage discharged from the Solotvyno area. Currently, the water of the watercourse flows into the reservoir and terminates there (Fig. 1). Therefore, it is an **inflow** reservoir. It should be noted that below the reservoir, the valley remains dry due to the interruption of the watercourse continuity.

PHYSICOCHEMICAL PROPERTIES OF RESERVOIR WATERS

The hydrochemical type and the concentration of the main cations and anions in the water of the "Solotvyno Lake District" reservoirs are diverse. The vast majority represent the di-ionic chloride-sodium type (Cl^--Na^+; Tab. 1). It is a consequence of rock salt leaching. Among all karst rocks, rock salt is one of the most soluble in water. The saturation limit is 360 $g \cdot dm^{-3}$ H_2O, temperature 20°C (Pulina, 1999). Therefore, most reservoirs are of this hydrochemical type. In reservoir No. 4, a sulphate-calcium type of water was found (SO_4^{2-}-Ca^{2+}; Tab. 1). It is the reservoir with the basin cut in clay, in which there are gypsum crumbs. Dissolving them enriches the water with sulphate and calcium ions, thus determining the hydrochemical type. The influence of the rock types in which the basin of the reservoir is cut is crucial in shaping the chemical composition of the waters (Molenda, Ciupa and Suligowski, 2020; Molenda and Kidawa, 2020). In a very shallow and recently created reservoir in the subsidence sinkhole (reservoir No. 8), a tri-ionic bicarbonate-chloride-sodium hydrochemical type (HCO_3^{2-}-Cl^--Na^+) was found (Tab. 1). It is related to the dominant role of surface and subsurface runoff in supplying the reservoir.

Although almost all reservoirs represent the same hydrochemical type of waters (except reservoirs No. 4 and 8), they show significant differences in water electrolytic conductivity (Tab. 1). Therefore, considering the salinity criterion proposed by Hammer (1986), the studied reservoirs can be classified into different types. The most numerous are subsaline ones with mineralisation of 0.5–3.0 $g \cdot dm^{-3}$ and hyposaline with mineralisation of 3–20 $g \cdot dm^{-3}$. These are reservoirs that were created in the **subsidence sinkholes**. The waters of these reservoirs do not come into direct contact with salt rocks and show a relatively low electrolytic conductivity (Tab. 1). These reservoirs are fed mainly with the precipitation waters and surface and subsurface runoff.

When the waters of reservoirs have direct contact with salt rocks, their waters show very high salinity. This case is represented by reservoir No. 2, the surface waters representing the mesosaline type (20–50 $g \cdot dm^{-3}$).

Secondary anthropogenic factors also influence the chemical composition of surface waters of reservoirs. It is particularly evident in reservoir No. 1, near the municipal waste landfill (Fig. 1). The inflow of leachate from the landfill causes, among other things, an increased concentration of ammonia (NH_4^+) and nitrite (NO_2^-) (Tab. 1). The waters of this reservoir are brown, which seriously limits the water transparency (SD ~ 0.4 m). Also, in reservoir No. 3, the inflow of sewage from the town of Solotvyno impacts the quality of its waters. An excellent indicator of the municipal sewage introduced into the reservoir is a high phosphate concentration (PO_4^{2-}), here with an average concentration of 0.6 $mg \cdot dm^{-3}$ (Tab. 1). In the surface layer (mixolimnion), it is a reservoir with advanced eutrophication processes, which is also expressed by the visibility of the Secchi disc <0.5 m and the concentration of chlorophyll *a* > 40 $\mu g \cdot dm^{-3}$. The concentration of chlorophyll *a* > 20 $\mu g \cdot dm^{-3}$ is considered typical for eutrophic reservoirs (Górniak and Kajak, 2020).

Among the ions, attention is also drawn to the very high concentration of calcium (Ca^{2+}), the average concentration of which in the bottom waters of reservoir No. 3 exceeds 1300 $mg \cdot dm^{-3}$. A similar, very high calcium concentration was also found in the hypersaline Kalush reservoir (Żurek *et al.*, 2018). The concentration of bromides (Br^-) is also very high. It is typical of most brines (Macioszczyk and Dobrzyński, 2002).

The differentiation of the physicochemical water properties in the vertical profile of the reservoirs is much more interesting. Reservoir No. 3 represents a considerable variation in those terms. The electrolytic conductivity increases with depth, but down to a depth of 14 m it does not exceed 9 $mS \cdot cm^{-1}$ (Fig. 4).

At 15 m, a distinct chemocline is visible, below which there is a monimolimnion layer with an electrolytic conductivity exceeding 200 $mS \cdot cm^{-1}$. The oxygen (Fig. 5) and redox conditions (Fig. 6) may also prove the permanent layer of water. In the near-surface layer, we observe water saturation with oxygen, which is a consequence of photosynthesis. "Water blooms" (Photo 3) and a very high concentration of chlorophyll *a* were found in the reservoir. There is a very rapid decrease in water oxygen saturation with depth, and at a few meters anaerobic conditions occur (Fig. 5). Huge differences also apply to the water pH; the difference between the surface layer and the bottom layer was as much as 3 pH units (Fig. 7). Such a distribution of selected physicochemical parameters proves the **meromictic** nature of the reservoir. A similar distribution of the analysed parameters was found in other meromictic reservoirs in the world (Hrdinka *et al.*, 2013, Molenda, 2014; Molenda, 2015). It is worth noting that the water of the bottom layer of reservoir No. 3 has a temperature of 14°C, which is higher than that of the surrounding waters (Fig. 8). The persistence of such anomalies results from a huge difference in water density. It is a characteristic feature of meromictic reservoirs (Molenda, 2014). In reservoir No. 5 meromictic conditions were also found, which is documented by the profiles of electrolytic conductivity, water saturation with oxygen, redox potential, reaction and temperature (Figs. 4, 5, 6, 7, 8). In the case of this reservoir, the monimolimnion layer covers about 3 m of water above the bottom. Meromictic reservoirs located in the temperate climate zone are very few and belong to the unique mycotic type (Molenda, 2014; Molenda, 2015). Therefore, the development and concentration of such a large group of anthropogenic meromictic reservoirs on a small area are unique globally.

Table 1. Physical and chemical properties of reservoir waters (mean ±standard deviation)

Reservoir No.	Layer	*EC* (mS·cm^{-1})	pH	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+	HCO_3^-	Cl^-	NO_2^-	Br^-	NO_3^-	PO_4^{2-}	SO_4^{2-}	Hydro chemical type
				mg·dm^{-3}												
1	surface[1]	1.55 ±0.88	7.6	46 ±6.2	10 ±1.4	241 ±36	3.3 ±0.5	0.9 ±0.7	210 ±25	303 ±77	0.45 ±0.23	0.2 ±0.1	0.8 ±0.8	0	41 ±12	Cl^--Na^+
2	surface[1]	31 ±2.2	7.4	289 ±118	45 ±25	4,968 ±3,209	7.2 ±3.2	49 ±45	140.52	7,296 ±5,078	5.0 ±5.9	3.2 ±2.9	22 ±31	8.4 ±11	207 ±56	Cl^--Na^+
3	surface[1]	1.62 ±0.25	7.9	59 ±27	11 ±2.5	259 ±103	8.5 ±4.2	2.8 ±3.8	199 ±86	346 ±168	0.49 ±0.36	0.17 ±0.25	8.4 ±6.2	0.34 ±0.2	60 ±17	Cl^--Na^+
	bottom[2]	220	6.8	1,709	291	106,270	141	0	357	159,575	2.1	13.6	32.4	0	1635	
4	surface[1]	1.93 ±0.86	7.5	259 ±95	116 ±43	31 ±12	6.2 ±2.2	0.47 ±0.32	139 ±44	18 ±9.5	0.8 ±0.6	0	2.5 ±2.2	0	960 ±431	SO_4^{2-}-Ca^{2+}
5	surface[2]	23	7.6	317	68	7,283	4.5	3.1	76	11,726	6.8	6.8	69	24	288	Cl^--Na^+
6	surface[2]	8.26	7.7	297	58	1,667	4.6	9.8	244	2,773	0	2.1	1	0	82	Cl^--Na^+
7	surface[2]	2.86	7.2	77	13	519	4.8	0.9	259	629	0	0.23	9	0	41	Cl^--Na^+
8	surface[2]	1.17	8.2	16	2.9	189	3.4	5.7	271	123	0.06	0.05	7.6	0	6.7	HCO_3^--Cl^--Na^+

[1] Six samples were taken. [2] Two samples were taken (due to extremely dangerous sampling conditions).
Explanation: *EC* = electrolytic conductivity.
Source: own study.

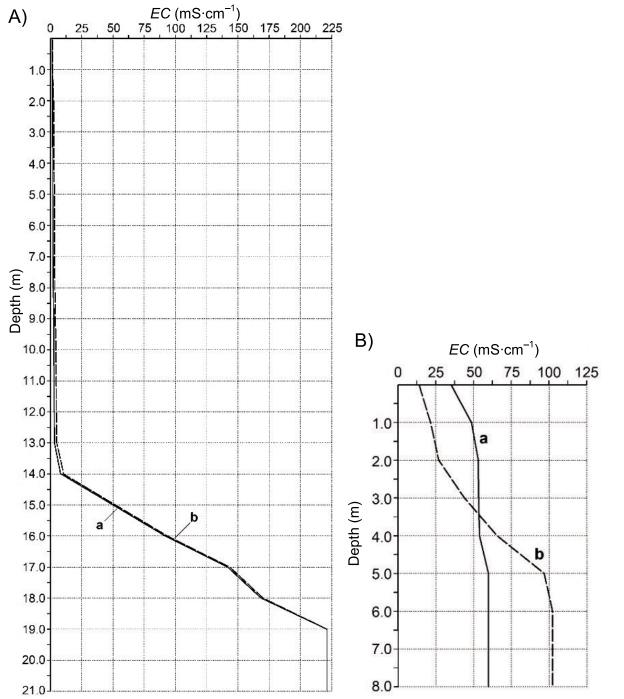

Fig. 4. Electrolytic conductivity (*EC*) profiles of the reservoirs: A) "Solotvyno No. 3", B) "Solotvyno No. 5"; *a* = summer 2020, *b* = spring 2021; source: own study

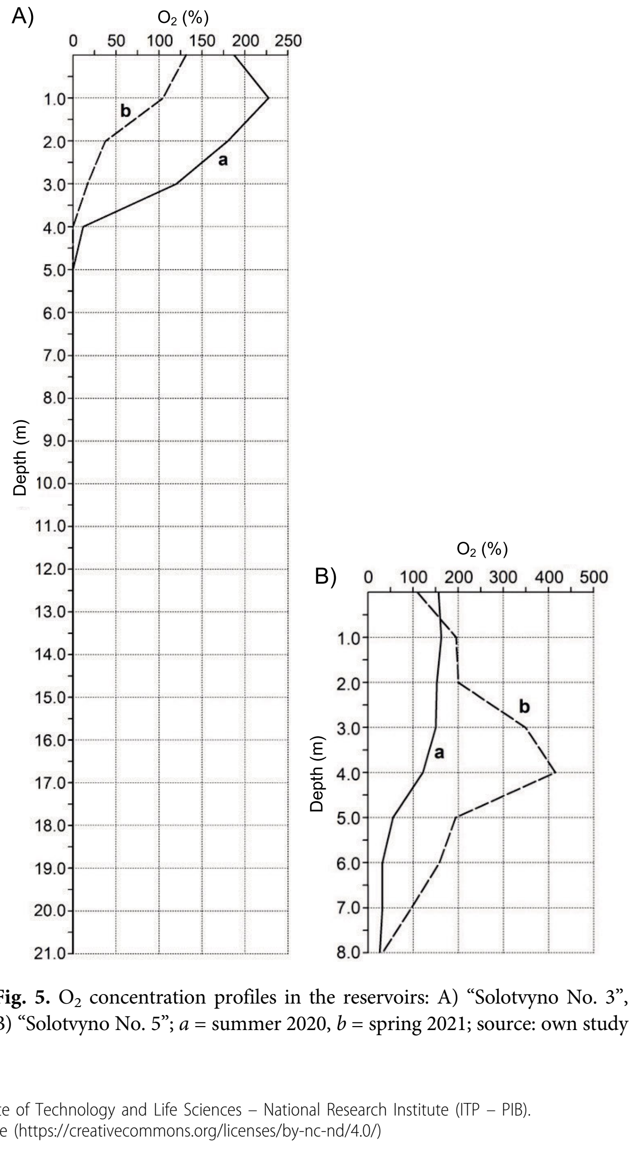

Fig. 5. O_2 concentration profiles in the reservoirs: A) "Solotvyno No. 3", B) "Solotvyno No. 5"; *a* = summer 2020, *b* = spring 2021; source: own study

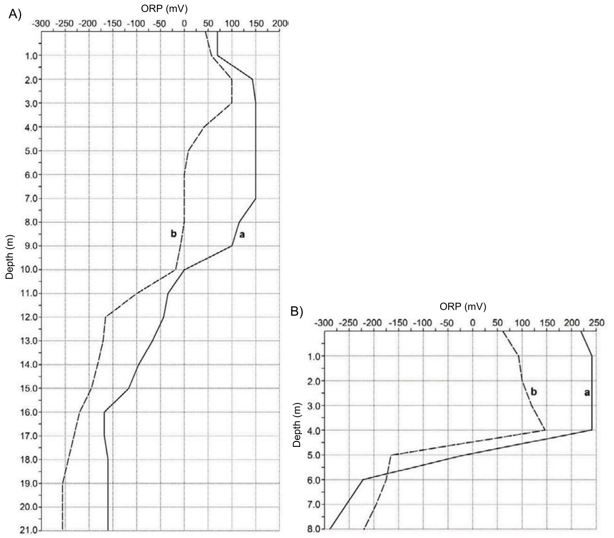

Fig. 6. Redox profiles in the reservoirs: A) "Solotvyno No. 3", B) "Solotvyno No. 5"; *a* = summer 2020, *b* = spring 2021; ORP = oxidation reduction potential; source: own study

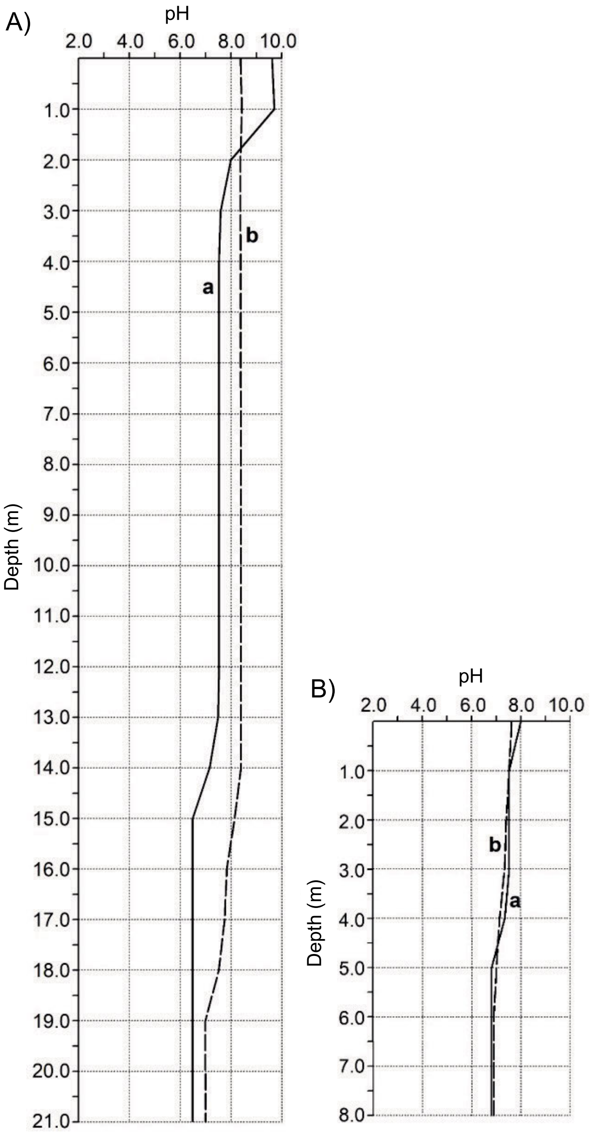

Fig. 7. pH profiles in the reservoirs: A) "Solotvyno No. 3", B) "Solotvyno No. 5"; *a* = summer 2020, *b* = spring 2021; source: own study

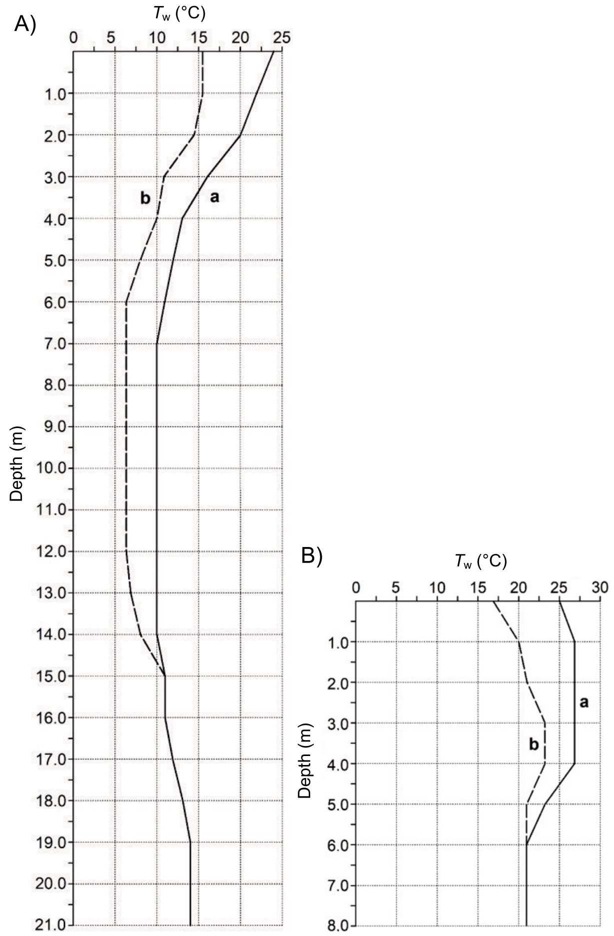

Fig. 8. Temperature (T_w) profiles in the reservoirs: A) "Solotvyno No. 3", B) "Solotvyno No. 5"; *a* = summer 2020, *b* = spring 2021; source: own study

SUMMARY AND CONCLUSIONS

The water disaster and flooding of the mines triggered the activation of anthropogenic and karst processes, which resulted in:

- changes in the layout of the surface hydrographic network (disappearance of watercourses) and destruction of the sewage network,
- the appearance of anthropogenic water reservoirs, which show:
  - various genesis (collapsed-corrosive, subsidence),
  - different physicochemical properties of waters both in the surface layer and in the vertical column (different hydrochemical types and salinity),
  - limited mixing processes (meromixing) with very well developed zones of mixolimnion, chemocline and monimolimnion,
- the presence of municipal waste landfills (mostly illegal) exposed the reservoirs to the secondary anthropogenic impacts leading to the eutrophication of their waters.

Eutrophication is manifested mainly by an increased concentration of biogenic elements, a high concentration of chlorophyll *a*, water blooms and a decrease in the visibility of the Secchi disc. The presented research has documented how a water disaster in a mine can change the water relations in mining areas. It also indicates the potential directions and threats resulting from anthropogenic and karst processes in other areas of **mining of chemical resources** in the world. It should be mentioned that the described processes may develop in all areas where mining of chemical raw materials takes place, regardless of the method of exploitation.

CONFLICT OF INTERESTS

All authors declare that they have no conflict of interests.

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