



A Study of a Hypersaline, Heliothermic Lake that Formed in an Anthropogenic-Karst Sinkhole

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Received: 15 July 2021 / Accepted: 10 June 2022 / Published online: 9 July 2022
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Abstract

In Solotvino, in southwestern Ukraine (Transcarpathia), there is a large group of anthropogenic water reservoirs. Most of these developed in sinkholes formed by the flooding of salt mines and the activation of anthropogenic and karst processes. One reservoir, Solotvino No. 7, was the subject of detailed limnological (hydrographic and hydrochemical) studies. The reservoir has an area of 8493 m², a maximum depth of 20.5 m, and holds Cl[−]–Na⁺ brines. The water in the near-surface layer is hyposaline (3–20 g/L), but periodically becomes mesosaline (20–50 g/L). Hypersaline waters with mineralization > 250 g/L are found below 3 m. The reservoir has three persistent distinct mixolimnion layers that clearly indicate their meromictic type: the surface layer, a chemocline (where the water chemistry changes), and a lower monimolimnion layer. The thermal properties of the reservoir deserve special attention. The water is heated during all seasons at the boundary between the chemocline and monimolimnion; the water temperature is 32 °C in winter and 54 °C in summer, despite the lack of volcanism. The water is heated by a physical phenomenon in the layer where the water density increases, which is a heliothermal process. Also noteworthy is that throughout the year, the oxygen profiles are positive and heterograde, with the water being up to 380% oxygen saturated.

Keywords Mining water · Hydrochemical type of water · Water pollution · Salinity · Meromixis

Introduction

Anthropogenic lakes formed due to mining undergo similar processes as natural lakes (Blanchette and Lund 2016; Molenda and Kidawa 2020). In most anthropogenic water lakes, the water's physicochemical properties are “balanced” and can be described as harmonious (Górniak and Kajak 2020; Rzętała 2008). The calcium bicarbonate (Ca²⁺HCO₃[−]) type of water is commonly dominant, and total mineralization does not exceed 0.5 g/L (Choiński 2000). Anthropogenic lakes can have different physical and chemical properties, such as extremely low or high pH (Czop et al. 2011; Hrdinka et al. 2013; Migaszewski et al. 2018a; Sanchez-España et al. 2008, 2020a, b), very high salinity (Molenda 2014, 2018; Żurek et al. 2018) or the presence of toxic substances, e.g. arsenic (Migaszewski et al. 2018b). Such reservoirs are described as disharmonious. The development of

anthropogenic reservoirs with extreme water environment properties is most often associated with mining activities, but so far, a relatively small number of such reservoirs have been studied (Górniak and Kajak 2020). Moreover, research in these reservoirs has focused mainly on the chemical composition of their surface waters. Reservoirs that differ in the chemical composition of their surface waters also show significant variability in their vertical and horizontal profiles (Bohrer et al. 2017; Molenda 2014; Molenda and Kidawa 2020; Sanchez-España et al. 2020a; Vandenberg and Litke 2018). We investigated the complex hydrographic and hydrochemical characteristics of a hypersaline, anthropogenic lake, focusing on the influence of the catchment's geological structure and seasonal vertical variability of the water's physicochemical properties.

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Methods

Study Site

Soltvino no. 7 Lake (hereafter called no. 7 Lake) is found in Transcarpathia (SW Ukraine, also known as Carpathian Ruthenia, Carpatho-Ukraine, or Zakarpattia), near the border with Romania (Fig. 1). The geology of the area consists of a salt dome. The dome ceiling reaches the ground surface, and in the 1970s, salt outcrops, called “salt mountains,” were still observed (the old photography of this region). The dome is elliptical in shape, with its longer axis in W–E direction and the shorter in N–S. The dome widens significantly with increasing depth. The dome's geology is complex, with the layers' steep decline, a characteristic of salt dome structures (Diakiv 2012).

No. 7 Lake is about 280 m above sea level, within the Tisza River's right-bank meadow terrace. The average annual air temperature of the area is 8.2 °C, with the lowest in January (−3.8 °C) and the highest in July (18.9 °C). The area's average annual rainfall is 1267 mm, with the highest in

July (134 mm) and the lowest in February (83 mm) (<https://pl.climate-data.org/europa/ukraina/obwod-zakarpacki-516/>).

In the Soltvino area, the salt deposits have been exploited since ancient times (Diakiv 2012). Deep salt mining within the Soltvino deposit was carried out in both room and room and pillar systems. The depth of the excavations from the ground surface reached a maximum of 400 m. At the end of the twentieth century, the deposit was accessed through several shafts. As a result of many years of exploitation, many large post-mining rooms were created. In 2008, there was a water disaster within the mines, and vast amounts of water (500–600 m³/h) began to flow into the workings. The inability to pump out such large amounts of water resulted in the workings gradually being flooded (Stoeckl et al. 2020). This in turn led to the activation of karst processes, resulting in rapid tightening of the rooms and destabilization of their walls and ceilings (Diakiv 2012). In an extreme case, the ceiling collapsed. The effects of these anthropogenic-karstic processes led to continuous (subsidence basins) and discontinuous deformations (sinkholes). Forms of this type are known from other salt extraction places, for example, in Russia and Poland (Andrejchuk 2002; Mycielska-Dowgiałło

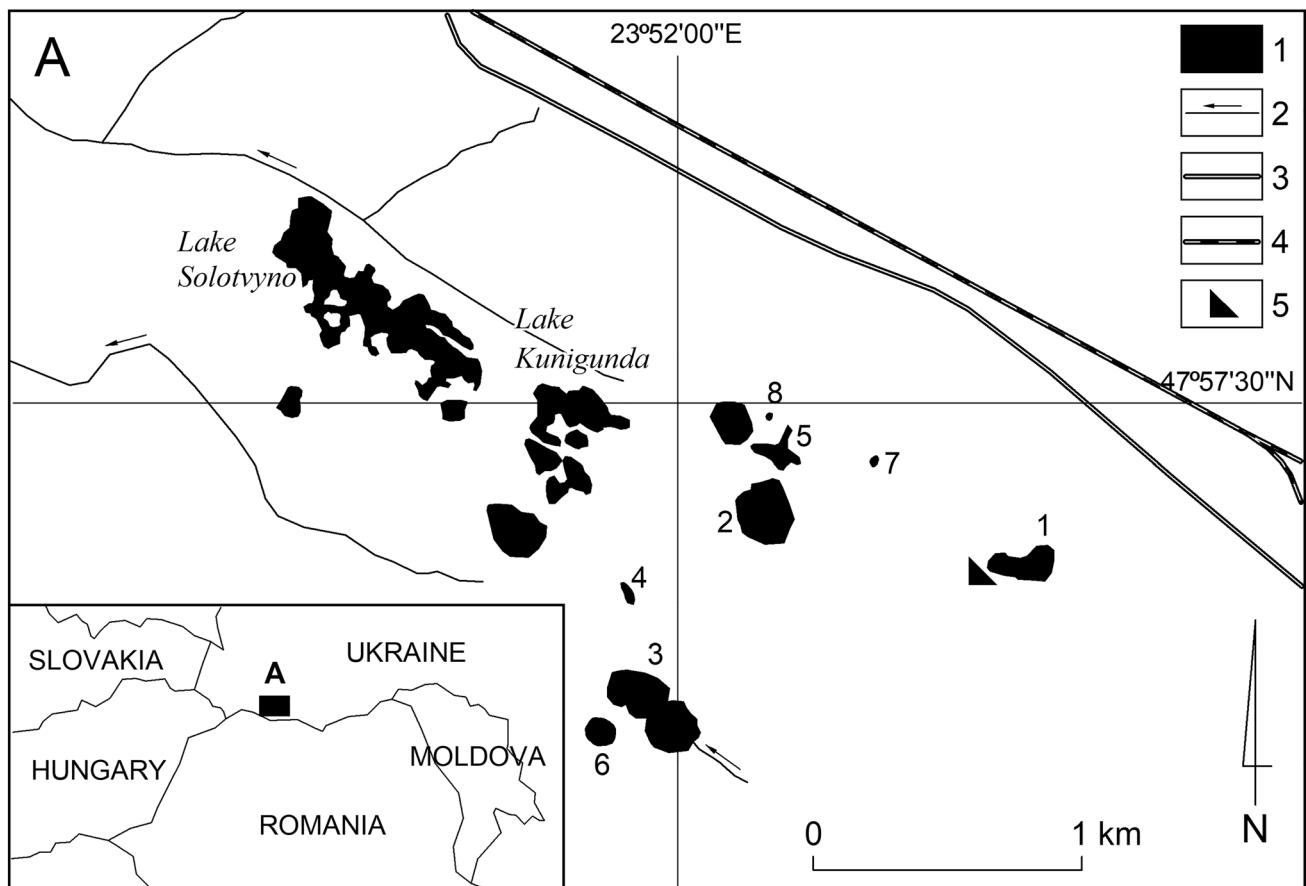


Fig. 1 Localization of investigated reservoirs: 1—anthropogenic reservoirs; 2—stream; 3—roads; 4—railway line

et al. 2001). In Solotvino, some of the resulting sinkholes were flooded. No. 7 Lake, one of these flooded sinkholes, is the focus of this paper.

Sampling

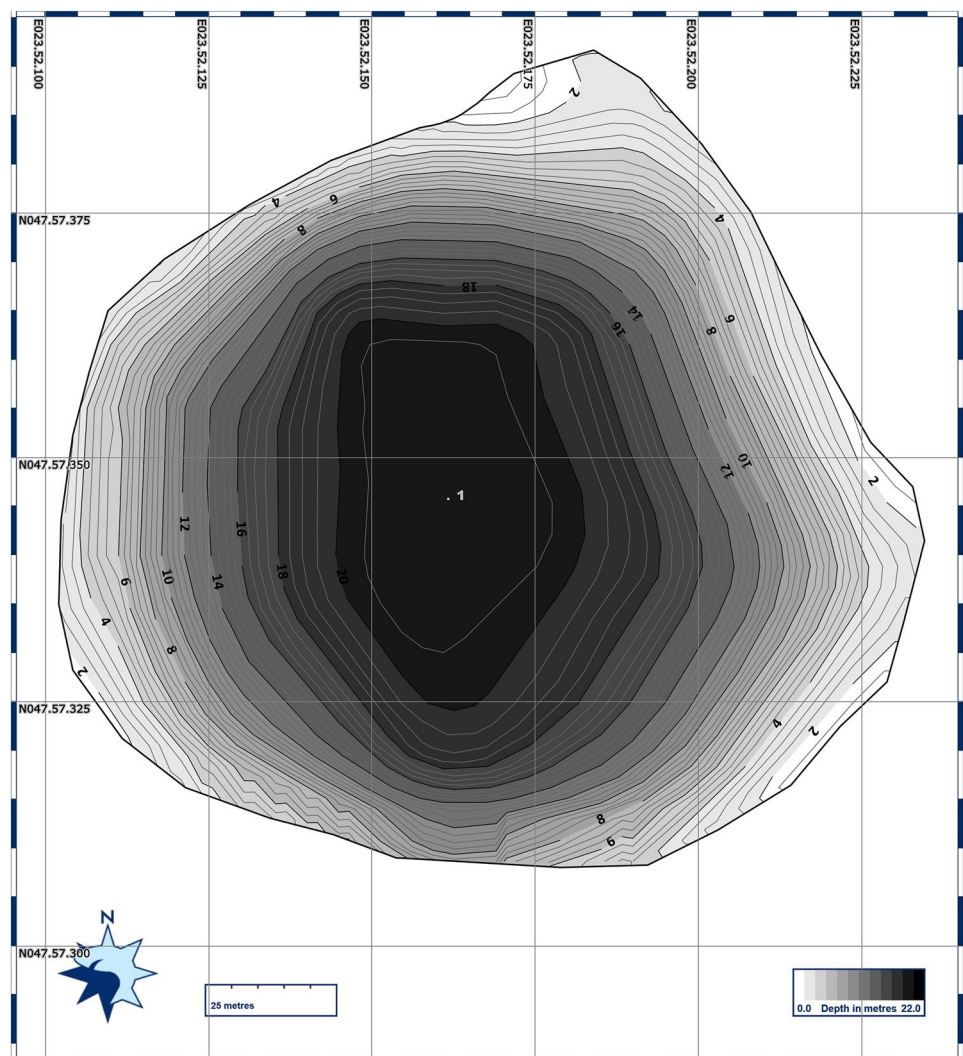
Hydrographic mapping was used to design the sampling locations in No. 7 Lake, per the guidelines provided by Gutry-Korycka and Werner-Więckowska (1996). Measurements of the lake depth were made from a boat using sonar Elite TI 2 (Lowrance, USA) with a built-in GPS receiver. Based on the measurements, a bathymetric plan was plotted using Reef Master 2.0 (Software Ltd., UK). Measurements of the above-water part of the sinkhole (width, depth, slope inclination) were made using a TruPulse 200 L laser range-finder (Laser Technology Inc., USA).

A sampling site in the center of the reservoir (Fig. 2) was reached by a pontoon boat. Access to the lake was achieved using mountaineering techniques (harness, rope). Basic

physicochemical parameters (temperature, pH, electrical conductivity (EC), and dissolved oxygen (D.O.) saturation) were measured in a vertical profile (at 1 m intervals) using a multi-parameter EDS 6600 probe by YSI (U.S. production), while transparency was measured with a Secchi disk (SD). Measurements were taken in spring (April 2019), summer (August 2019, July 2020), autumn (November 2019), and winter (February 2020).

Water samples for chemical analysis were collected at the lake's surface (0.1 m) using a telescopic boom and at its bottom using a Van Dorn sampler (Wildco Science First, USA). Water samples were stored in polyethylene bottles and transported at about 4 °C. Before analysis, the samples were filtered through a 0.45 µm filter (Millipore). 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^- , NO_3^- , and PO_4 using 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

Fig. 2 Bathymetric map of the “Solotvino No 7” reservoir: 1 points of sampling



0.7 mM dipicolinic acid, and 1.7 HNO_3). Bicarbonates (HCO_3^-) were determined by titration with the basicity index b–r (blue–red).

Results and Discussion

Hydrographic Conditions

No. 7 Lake formed following the collapse of the salt post-exploitation room (Fig. 3). The lake's slopes are built of loose fluvial sediments (sand, gravel, and pebbles). These are the sediments of the meadow terrace of the Tisza River. Below the layer of fluvial sediments, there is a layer of grey eluvial clays lying on the rock salt. The sinkhole basin was filled with rainwater and drainage waters from the Quaternary level (Fig. 3). The Quaternary aquifer is 15–20 m below the ground surface. Concentrated outflows of these waters were found in some places of the reservoir's cap, where they emerge at the contact of sandy-gravel sediments with the clay (Fig. 3). The reservoir is also supplied by direct precipitation. With an average annual rainfall of 744 mm and a reservoir area of 18,493 m^2 , direct rainfall provides $\approx 23,000 \text{ m}^3$ of freshwater per year. In terms of hydrology, it

is a retention-and-evaporation basin. No watercourse flows into or out of this endorheic reservoir.

The reservoir basin has the form of a truncated cone. The reservoir's underwater slopes are steep and the bottom is flat (Fig. 2), with a maximum depth of 20.5 m. The bottom sediments are sands and gravels displaced from the layers above (Fig. 3). The height of the sinkhole's edge above the water table ranged from 9.8 to 30.8 m, with a slope of 35–45°. This is a typical slope for sinkholes formed in loose rock (sand, gravel), which is generally dictated by mass movements, mainly sliding rock material (Figs. 4, 5; Durica et al. 2008). Around the edge, some landslides have occurred, resulting in very steep ($\approx 90^\circ$) edges. Landslides are slowly reducing the volume of the lake, in a similar way to another anthropogenic-karst sinkhole in the Ural Mountains, Russia (Andrejchuk 2002). Numerous wooden beams, fragments of the housing of the old mining tunnel, float on the surface of the reservoir. Due to the water's very high salinity, no aquatic vegetation was found.

Physicochemical Properties of the Water

The lake waters were typical chloride–sodium type (Cl^- – Na^+) brines (Table 1), due to the dissolution of salt rocks by water flowing into the sinkhole. The lake basin's

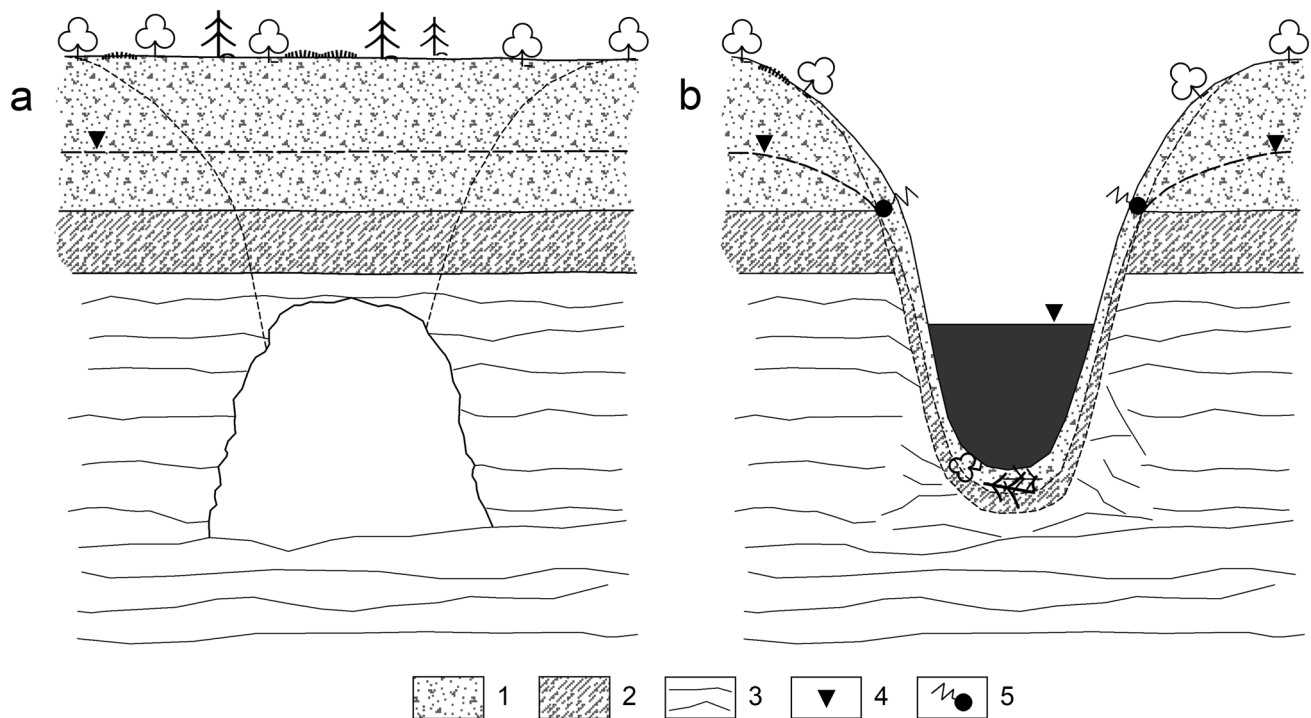


Fig. 3 Scheme of creating a water reservoir: 1—sand and gravel; 2—clay; 3—salt; 4—groundwater table; 5—source

Fig. 4 “Solotvino No 7” reservoir in the anthropogenic sinkholes (Ukraine)



Fig. 5 Shore zone of the reservoir “Solotvino No 7”

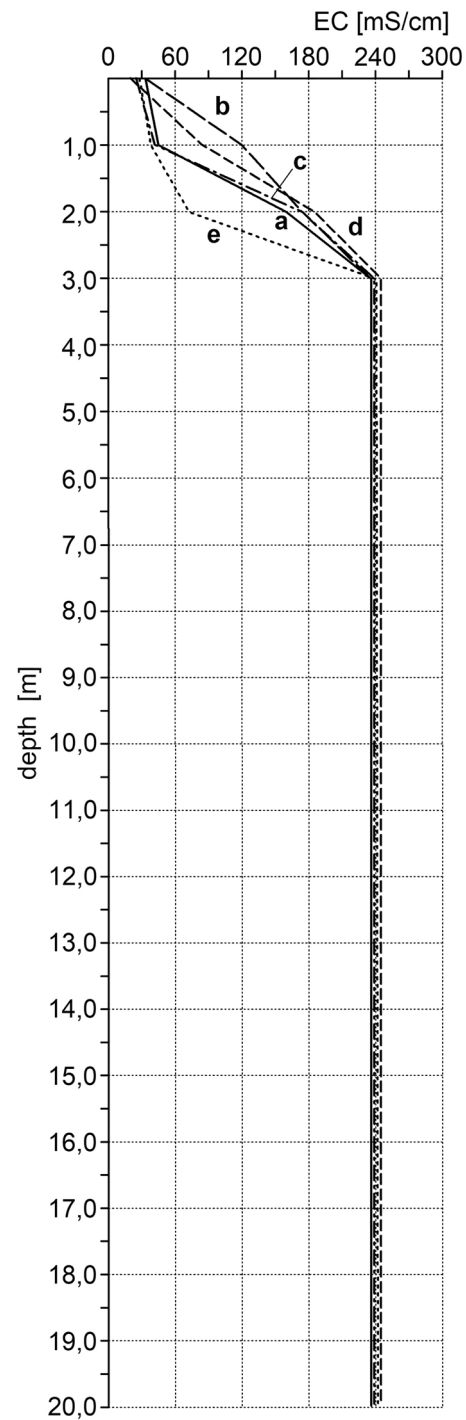


geology decisively influences the lake waters' hydrochemical type (Castendyk et al. 2015a, b; Molenda and Kidawa 2020). Chloride–sodium dominated water can also occur in

other anthropogenic lakes, for example, post-mining, where the raw material was potassium salt (Żurek et al. 2018) and lakes into which saline mine waters are discharged (Molenda

Table 1 Means of chemical parameters with the standard deviation (in parentheses) of waters in studied reservoir in mg/L ($n=5$)

Measurement point	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	NH ₄ ⁺	HCO ₃ ⁻	Cl ⁻	NO ₂ ⁻	Br ⁻	NO ₃ ⁻	PO ₄ ²⁻	SO ₄ ²⁻
Surface layer [0.1 m]	289.5 (118)	45.0 (25)	4968 (3209)	7.2 (3.2)	49 (45)	140.2 (52)	7296 (5078)	5.0 (5.9)	3.2 (2.9)	22 (31.8)	8.4 (11)	207.2 (56)
Layer above the bottom [20 m]	1232.4 (24)	90.2 (3)	116,857 (2571)	65.6 (6.5)	362 (33)	239 (5.1)	168,969 (4049)	0.0	12.7 (0.9)	3.6 (0.2)	0.0	1784 (2.6)

**Fig. 6** Electrical conductivity (EC) profiles of the “Solotvino No 7” reservoir: **a** Spring 2020; **b** Summer 2019; **c** Autumn 2019; **d** Winter 2020; **e** Summer 2020

2014, 2018). There was a large difference in the concentration of the primary ions between the surface water and bottom layer (Table 1). According to the Hammer classification (1986), the near-surface layer (≈ 0.1 m) water can be classified as hyposaline (3–20 g/L), periodically changing

into mesosaline waters (20–50 g/L), with hypersaline waters below 3 m. Sodium and chloride ions dominated due to rock salt (halite) leaching. Halite is one of the most soluble rocks, with a saturation limit at 25 °C as high as 363 g/L (Pulina 1999). There were also very high concentrations of Ca^{2+} in the bottom water (an average of 1232 mg/L). Similarly, very high concentrations of Ca^{2+} were found in the hypersaline Kalush reservoir (Żurek et al. 2018). Like most brines, bromide (Br^-) concentrations were also very high (Macioszczyk and Dobrzyński 2002).

Water transparency in the reservoir ranged from 2.6 to 4.2 m and was primarily influenced by falling rock material (Fig. 4) and landslides, which introduced a great amount of fine-grained mineral fractions into the lake. For example, in spring 2019, following a landslide, water transparency decreased to 2.6 m. Periods of intense rainfall likely also affected water transparency, as fine-grained material lying on the slopes of the sinkhole was washed into the water. The influence of intense precipitation causing turbidity and, consequently, a decrease in transparency, has been noted in other lakes (Choiński 2000).

We observed an increase in the water's EC with depth (Fig. 6). The mixolimnion zone had the most variability in EC and individual ions concentration (Fig. 6, Table 1). The high variability is mainly due to the inflow of atmospheric precipitation, surface runoff from the reservoir's immediate catchment area, and fresh groundwater. This leads to the periodic dilution of the brines and a decrease in EC. In more extended periods without precipitation or strong winds, brines from the deeper layer rise towards the surface,

which increases the EC. Many other anthropogenic saltwater reservoirs show these phenomena (Molenda 2015, 2018). Below 3 m, there is a monimolimnion layer. The EC and the chemical composition of this layer's waters are very stable, with an annual cycle that is typical of other meromictic (permanently stratified) reservoirs (Boehrer et al. 2017; Hrdinka et al. 2013; Molenda 2015).

A large difference in the EC of the surface layer water found by Stoeckl et al. (2020), which came from research conducted in 2016 and the present one. Then, the EC of the water was ≈ 250 mS/cm, and in the surface layer, it was ≈ 300 mS/cm. At that time, there were blocks of rock salt in the reservoir and its coastal zone, which were subject to intense dissolution and caused the high mineralization. The more recent bathymetric measurements revealed no salt blocks in the reservoir or its coastal zone. In addition, brine is being intensively pumped at a depth of 2–3 m (the warmest waters) to supply the swimming pools in the “Solotvino Resort” (Fig. 7). This loss of brine causes an influx of freshwater from the Quaternary level, along with further dilution by fresh atmospheric precipitation. Given that the roof layers and sides of the mining chamber have already completely dissolved, the EC is gradually decreasing. The current values of EC in the surface layer oscillate around 30 mS/cm.

Considering the classification proposed by Boehrer and Schultze (2006), the lake was ectogenic meromictic. Anthropogenic meromictic lakes are unusual hydrographic features, especially in temperate latitudes. The massive difference in the mineralization of the waters between the subsurface layer and the monimolimnion waters would naturally induce

Fig. 7 Location of pumps in the reservoir



meromixis. In addition, the depth coefficient (Z_r) predisposes this reservoir to meromixis. A value above 8% significantly hinders mixing water processes (Hongve 2002), but in this reservoir, the depth coefficient (Z_r) is 13%. The form in which the reservoir is located is also essential. The deep embedding of the reservoir in the anthropogenic-karst sink-hole significantly reduces the effect of wind on the water surface. Similar conclusions were drawn when examining reservoirs formed in submerged granite quarries (Molenda 2015).

No ice forms in the lake, due to both the water's very high salinity and some very noteworthy thermal phenomena. There is a very distinct increase in water temperature in all seasons at a depth of 2–3 m, i.e. at the chemocline and monolimnion boundary (Fig. 8). In August 2019, at a depth of 2 m, the water temperature reached 53.9 °C. This is unique for lakes not associated with volcanic areas. In July 2020, the temperature was lower (47 °C), while in winter it was 32 °C. Solar heat accumulates in the dense water layer, as described by Weinberger (1964) and Hull (1979); this has also been recorded in other anthropogenic saltwater reservoirs (Chonka et al. 2013; Molenda 2014, 2018; Stoeckl et al. 2020; Żurek et al. 2018) and natural lakes (Alexe and Serban 2014). However, such high temperatures (> 30 °C) have never been sustained throughout the year elsewhere except in geothermally heated lakes, such as Heviz in Hungary or Rotowhero in New Zealand, where the high-water temperature is a consequence of the lakes being fed by hot springs (McCull and Forsyth 1973). In the case of the No. 7 reservoir, it is a consequence of the physical process in the zone of increased water density. In the monolimnion layer below 11 m, the temperature throughout the year is stable at 17 °C (Fig. 8). The same phenomenon and temperature (18 °C) were found in the hypersaline Dombrovska lake in Kalush (Żurek et al. 2018).

In all seasons of the year, the surface oxygen profiles reveal a positive (+) heterograde, and oxygen supersaturation of water reaches a maximum of 380% (Fig. 9). Even in winter, the water is supersaturated with oxygen at 148%. Supersaturation with oxygen has also been found in other extremely meromictic lakes, in association with phytoplankton (Hrdinka et al. 2013), and the highest degree of supersaturation in the No. 7 reservoir occurred in summer, in the photic zone, suggesting that phytoplankton might be responsible. The oxygen saturation decreases with depth, and at the bottom was < 5%. Such a vertical distribution of water oxygen saturation is characteristic of most meromictic lakes (Hrdinka et al. 2013; Molenda 2014). Low oxygen saturation of monolimnion waters or its complete absence results from the waters' permanent stratification, resulting in poor transfer of oxygen from the surface as well as biotic respiratory demand.

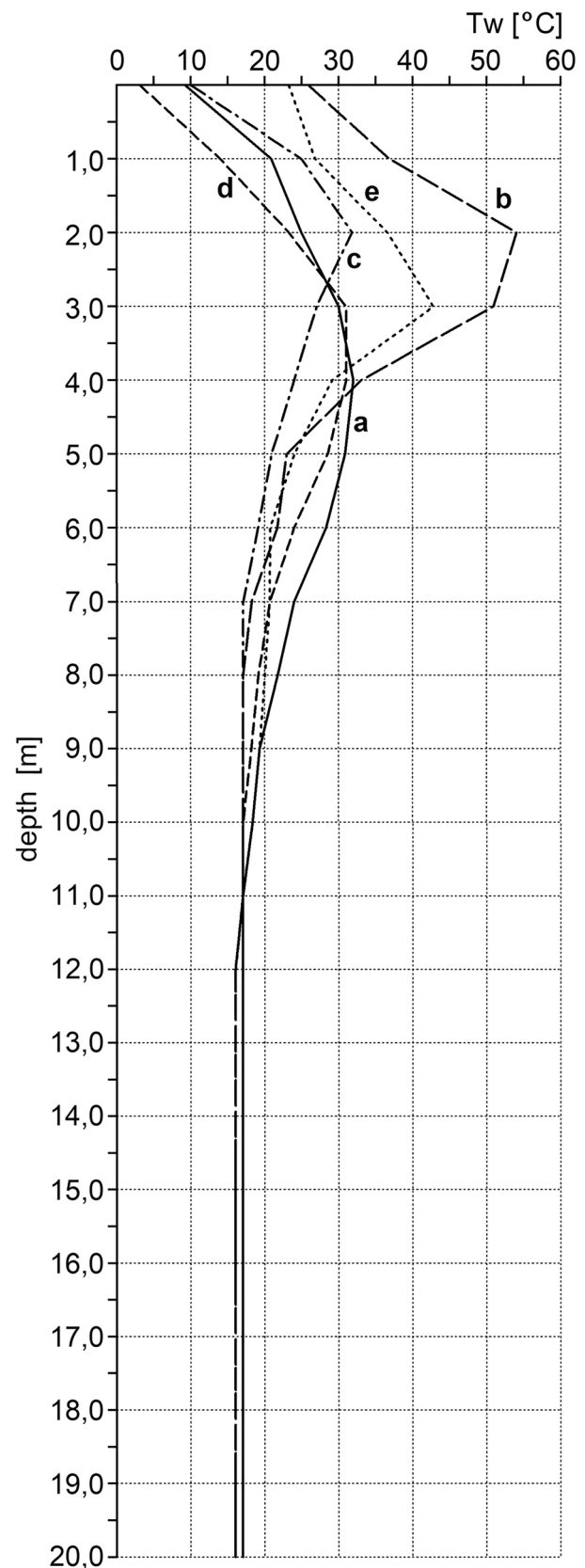


Fig. 8 Temperature profiles in the “Solotvino No 7” reservoir: **a** Spring 2020; **b** Summer 2019; **c** Autumn 2019; **d** Winter 2020; **e** Summer 2020

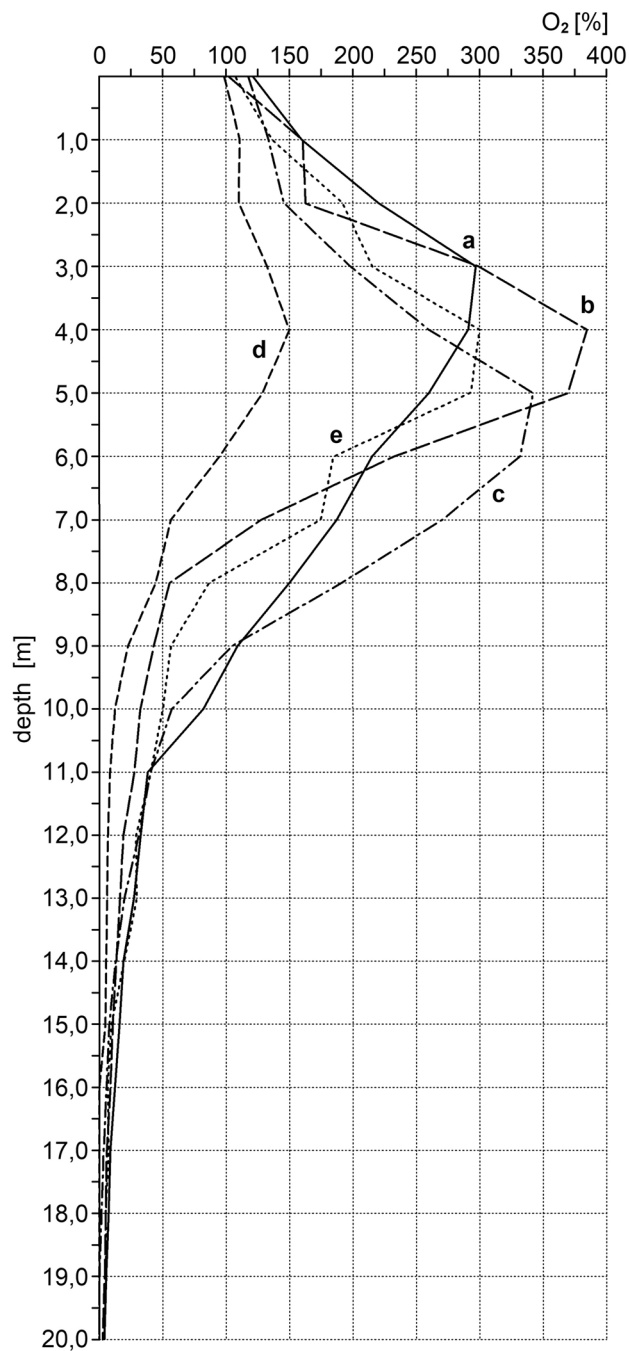


Fig. 9 O₂ concentration profiles in the “Solotvino No 7” reservoir: **a** Spring 2020; **b** Summer 2019; **c** Autumn 2019; **d** Winter 2020; **e** Summer 2020

Mixolimnion waters were slightly alkaline with a maximum pH value of 8.2. With depth, the pH decreased quickly; below 3 m, it was stable at about pH 5.9. The average redox potential of the mixolimnion waters was +226 mV, while the monimolimnion water had a redox potential of +284 mV.

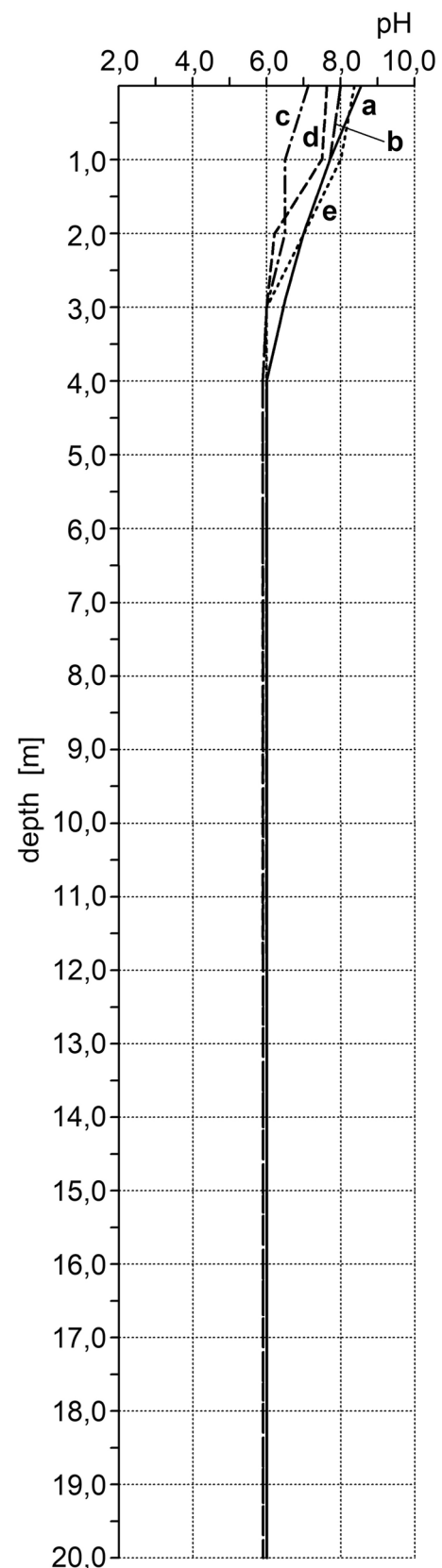


Fig. 10 pH profiles in the “Solotvino No 7” reservoir: **a** Spring 2020; **b** Summer 2019; **c** Autumn 2019; **d** Winter 2020; **e** Summer 2020

Thus, oxidizing conditions prevail in the reservoir's entire vertical column (Fig. 10).

Summary and Conclusions

Given the genesis and the annual variability/stability of the reservoir's waters' physicochemical properties, the anthropogenic-karst No. 7 lake can be considered one of the world's most unique disharmonious reservoirs. Formed in a sink-hole with a truncated cone, the hypersaline lake is a meromictic, heliothermal lake (with the water temperature at the chemocline/monimolimnion boundary $> 30^{\circ}\text{C}$ throughout the year), which is due to physical phenomenon rather than water inflow from hot springs. The water's physicochemical properties are highly variable in the mixolimnion and very stable in the monimolimnion, with no freezing (due to the water's high salinity and heliothermal warming).

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