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TECHNICAL ARTICLE

Unique Pit Lake Created in an Opencast Potassium Salt Mine (Dombrovska Pit Lake in Kalush, Ukraine)

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Abstract
We studied the physicochemical and biological characteristics of the Dombrovska pit lake in Ukraine. The lake formed in an abandoned opencast potassium salt mine and is one of the most saline inland water bodies in the world. It is 85 m deep (November 2015) and an annual inflow of about 2 Mm^3 of water. The lake has two distinct layers. The mesohaline surface (0–5 m) layer is well oxygenated and slightly alkaline (pH = 7.5–8.8). Its mineralization, expressed as dry mass, was 50–134 g dm^{-3}, and its electrical conductivity (EC) was 58–134 mS cm^{-1}. The underlying layer consists of hypersaline water with low amounts of dissolved oxygen, a neutral pH (6.7–7.4), high mineralization (179–420 g dm^{-3}), high EC (169–215 mS cm^{-1}), and higher concentrations of major anions and cations (except Ca^{2+}) and nutrients than the overlying water. The vertical relationship between major ions and metals and the future salinity of the lake are discussed. In terms of zooplankton, in July we found living specimens of the rotifer *Brachionus plicatilis* and the ciliates *Paradileptus elephantinus* and *Tindinnidium* sp. as well as dead rotifers, cladocerans, and copepods (in total, 19 species), but only live *B. plicatilis* and 9 dead species in November. In the littoral part of the pit lake, we found the diatoms *Nitzschia pusilla* and some *Halamphora* species (*H. borealis, H. tenerrima, H. acutiuscula*), which favour highly saline waters.

Keywords Water chemistry · Metals · Protozoans · Diatoms · Zooplankton

Introduction

Potash resources come from marine deposits and usually occur deep in the earth. They are typically exploited by conventional shaft mining, dissolution mining, or evaporation from brines. In contrast, the potash ore that occurs near the city of Kalush in the Ukraine (Ivano Frankiv region, Carpathian Foredeep Basin), is located only about 20 m below the surface and is suited to opencast mining (Gaydin 2011). The ore is rich in kainite (KMg $(Cl/SO_4)\cdot 3H_2O$), halite (NaCl), and langbeinite ($K_2Mg_2(SO_4)_3$).

The Dombrovska open pit mine in Kalush operated from 1967 to 2005. More than 14.7 million tons of potassium salts with an admixture of NaCl were mined up to the 1990s. Mine closure occurred between 2005 and 2008, and included a groundwater collection ditch with a length of 5.3 km and a depth of 25 m dug around the opencast mine. Groundwater was pumped from the ditch to the nearby Sivka River. In 2008, due to bankruptcy of the enterprise, the opencast mine was abandoned and it filled with highly mineralised quaternary water, rain water, and groundwater seepage (Gajdin et al. 2014; Gaydin 2011). Because potassium and sodium salts are highly soluble (360 g kg^{-1} of water at 25 °C for both KCl and NaCl), they are naturally concentrated in the pit lake water, creating a unique water chemistry and specific life conditions for biota.

According to Dolin et al. (2010), the Dombrovska pit lake was expected to be saline throughout the whole water column, with water mineralization of 80–115 g dm^{-3} in the surface layer and ca. 400 g dm^{-3} at a depth of 10–15 m. In contrast, Gajdin et al. (2014) and Gaydin and Diakiv (2010) suggested that, based on physical modeling and theoretical calculations, the filled pit lake would have a freshwater surface layer (up to a depth of 18 m) and saline water only in the deeper layers. In this study, we investigated the chemical composition of the water and the biological life

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(zooplankton, diatoms). Based on the available literature, we hypothesised that the water chemistry would change as suggested by Gajdin et al. (2014) and Gaydin (2011) with the upper layer of the pit lake becoming less saline.

Materials and Methods

Study Area

The geological profile of the potassium salt deposit includes three basic substances: potash, salt-bearing breccias of weathered clays, and Quaternary formations. The salts include very soluble halite, kainite, and sylvite, and less soluble langbeinite, kieserite, polyhalite and anhydrite. The salt-bearing breccia consists of clays and sandstones (15–17%) bounded by halite, and contain up to 45% salt. The Quaternary sediments include 2–18 m thick water-bearing gravel layers covered by loams with a thickness of 2.5–6 m. In the southern part of the pit, the slopes consist of salt-bearing breccias and, in the northern part, potash (Fig. 1a, b; Gajdin et al. 2014).

The Dombrovska pit lake is located near the town of Kalush, Ukraine (49°01′34.18″N, 24°19′24.74″E). In November 2015, the lake was 1770 m long, 260–450 m wide, and 85 m deep (Fig. 2). Presently an annual inflow is about 2 million m^3 of water every year, causing an annual water level increase of about 4 m (Dolin et al. 2010). The pit lake has already accumulated over 20 million m^3 of brine. The slopes of the pit lake include the salt-bearing layer and the clay cap. The salinity is increased by occasional landslides of the clay and Quaternary gravels that cover the shore (Gajdin et al. 2014). The pit lake bottom is covered by a 20 m thick layer of clay.

Sample Collection and Methods

Water samples were collected in 2015 from one station situated at the deepest part of the pit lake. In July, we sampled at depths of 0, 5, 10, 15, 20, 30, 40, 50, 60, 70, and 80 m and in November, at depths of 0, 2.5, 5, 7.5, 10,

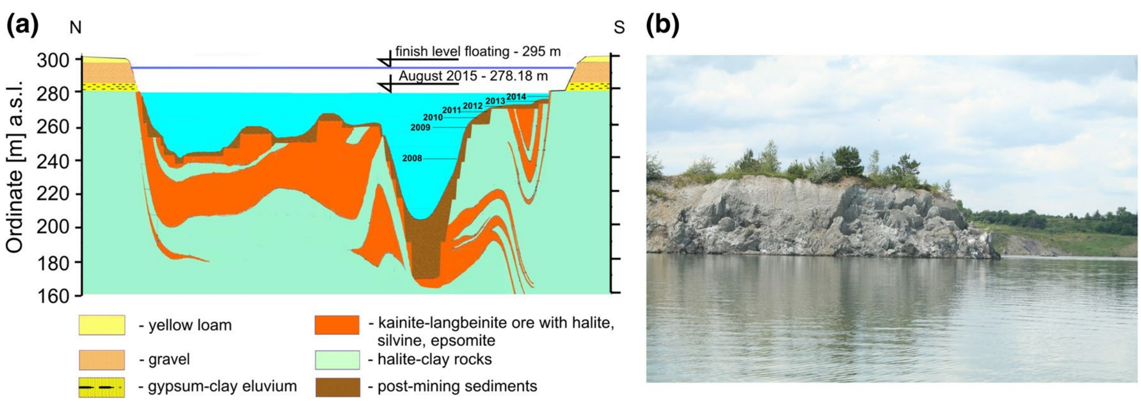
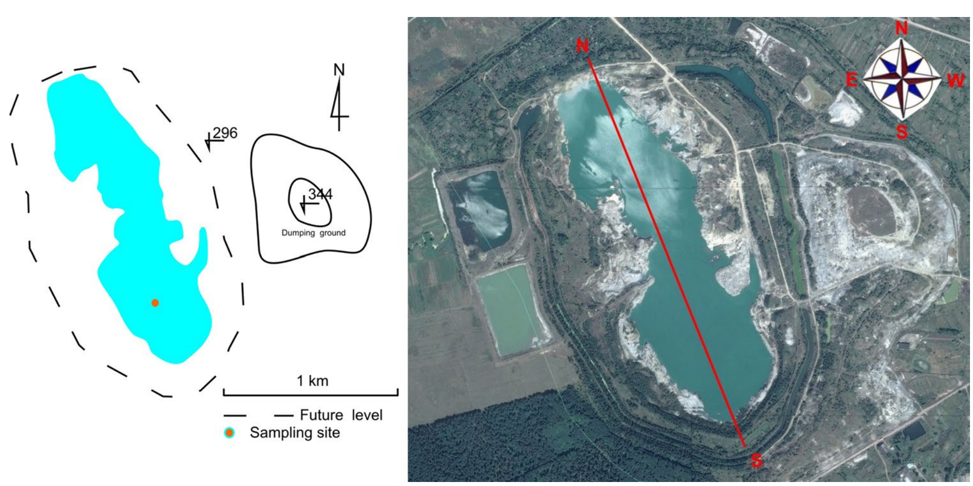


Fig. 1 **a** Geological cross section of the Dombrovska pit lake; **b** landslide of gypsum–clay eluvium

Fig. 2 Sketch of flooding pit of the opencast potassium salt mine Dombrovska and the location of the sampling points in the pit lake



15, 20, 30, 40, 50, 60, 70, 80, and 85 m. We determined the following parameters: pH, electrical conductivity (EC), water mineralization, dissolved oxygen (DO), oxygen saturation, and concentrations of anions (Cl^-, SO_4^{2-}, HCO_3^-, NO_3^-), cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+), and metals (Cd, Pb, Zn, Mn and Fe).

The EC and pH were analysed in situ. The concentrations of inorganic ions (Cl^-, SO_4^{2-}, HCO_3^-, NO_3^-, Na^+, K^+, Ca^{2+}, Mg^{2+}) were analysed using ion chromatography (DIONEX ICS 1000 and IC DX 320). Due to the high EC levels, this analysis required considerable dilution (100 and 500×) of the water samples. Therefore, the data for those anions that were present in lesser amounts at certain depths were below the detection limit. Water mineralization was expressed by the amount of dry residue. Light conditions were determined in July using a Secchi disk. The Winkler method was used to determine DO. For metal analysis, samples were acidified to $pH < 2$ with ultrapure HNO_3. The concentrations of Zn, Cd, Pb, Fe, and Mn were measured using a Varian Spectra AA-20 atomic absorption spectrophotometer with atomization in an air-acetylene flame. Chlorophylls were extracted from membrane filters after filtering a known volume of lake water and analysed in 90% acetone at 630, 663, 664, and 647 nm using a spectrophotometer U-1900 with a slit width of 4 nm and a path length (cuvette) of 10 mm. Chlorophylls *a* and *b* were calculated using the formulas described in Mitchel and Kiefer (1984) for mixed phytoplankton and chlorophyll *c* was calculated using the formula for cryptomonads and dinoflagellates: chlorophyll $c = 27.09\ E_{630} - 3.63E_{663}$, where E_{630} and E_{663} are the solution extinction at 630 or 663 nm, respectively.

Because we detected a strong hydrocarbon odour in the deeper water layers, we analysed hydrocarbons in the water samples from 85 to 50 m deep. The analysis was performed by gas chromatography CLARUS 500 with an FID detector according to norm PN-EN ISO 9377-2:2003. For the extraction of oil from water samples, the solvent *n*-hexane in HPLC grade was used.

Water for biological analysis was taken using a 5 L bathometer from the same depth as the water for physicochemical analyses. We filtered the 15 L water samples through a #50 µm planktonic net. In the first sampling term (July), samples were preserved with 4% formalin. During the second sampling term (November), planktonic samples were not preserved until identification of living organisms was complete. This procedure was due to the difficulty of distinguishing between as-sampled living and dead animals in a preserved sample. Taxonomic identification of ciliates (Ciliata) was carried out in the living material in a water drop with cover glass according to Foissner and Berger (1996) and Foissner et al. (1999). Identification of rotifers (Rotifera), cladocerans, and copepods was carried out using several identification keys (Bielańska-Grajner et al. 2014; Dussart 1969; Flössner 1972; Koste 1978).

Diatoms were determined in the benthic sample of surface sediment covered by algae collected ca. 0.2 m from the shore. The diatoms were identified with a Nikon 80i light microscope on permanent slides, where diatom valves were mounted using the synthetic resin Naphrax®. Diatom identification was based mainly on Krammer and Lange-Bertalot (1986, 1988, 1991, 2004).

Pearson linear correlations were used to estimate the relationship between environmental parameters. The Wilcoxon test was used to determine differences in the water column's physicochemical parameters between July and November.

Results

Physicochemical Water Parameters

Light conditions were poor in the Dombrovska pit lake in July, with a Secchi depth of only 0.8 m, indicating a euphotic zone of about 2 m. The water temperature varied with depth (Fig. 3). In July, the temperature was high (22–23 °C) at the near-surface water and at ≈ 10 m depth, while the lowest observed temperature in July (14.9 °C) was at a depth of 5 m. Temperature showed little variability (17.0–20.3 °C) below a depth of 10 m. In November, the lowest temperature was at the surface (7.4 °C) while the highest temperature (22 °C) was observed at a depth of 10 m, unchanged from the July reading. Between the depths of 15 and 85 m, water temperature was almost constant (17.1–17.5 °C).

Water pH ranged from 6.7 to 8.0 (Fig. 3). Surface water layers (0–5 m) were slightly alkaline ($pH > 7.5$), but from depths of 15–85 m, the pH was in the neutral range (6.8–7.4). We observed a gradual increase in pH from 10 m and deeper in July and small changes in November. The pH values were significantly higher in July than in November (Table 1). The DO in the pit lake water ranged from 0.2 to 10.9 mg dm^{-3} (Fig. 3). Surface water layers (0–2.5 m) were well oxygenated, while the deeper layer (15–80 m) were poorly oxygenated (oxygen saturation > 90% and 1.4–6.9%, respectively). The concentrations of DO and oxygen saturation was positively correlated with pH (Table 2).

The EC values (58–215 mS cm^{-1}) indicated high mineral salt concentrations in the pit lake water. The concentrations of major anions and cations in the water were in the following ranges (in g dm^{-3}): 19–167 for Cl^-, 5.4–78.6 for SO_4^{2-}, 0.3–6.1 for HCO_3^-, 15.2–125.3 for Na^+, 2.0–35.3 for K^+, not detected (nd)–0.6 for Ca^{2+} and 1.3–27.8 for Mg^{2+}. Vertical profiles of Cl^-, SO_4^{2-}, Na^+, K^+ and Mg^{2+} concentrations in the pit lake water were similar (Fig. 3). They were lower in the surface water layer (0–5 m) and then gradually increased towards the bottom. They were similar or lower at

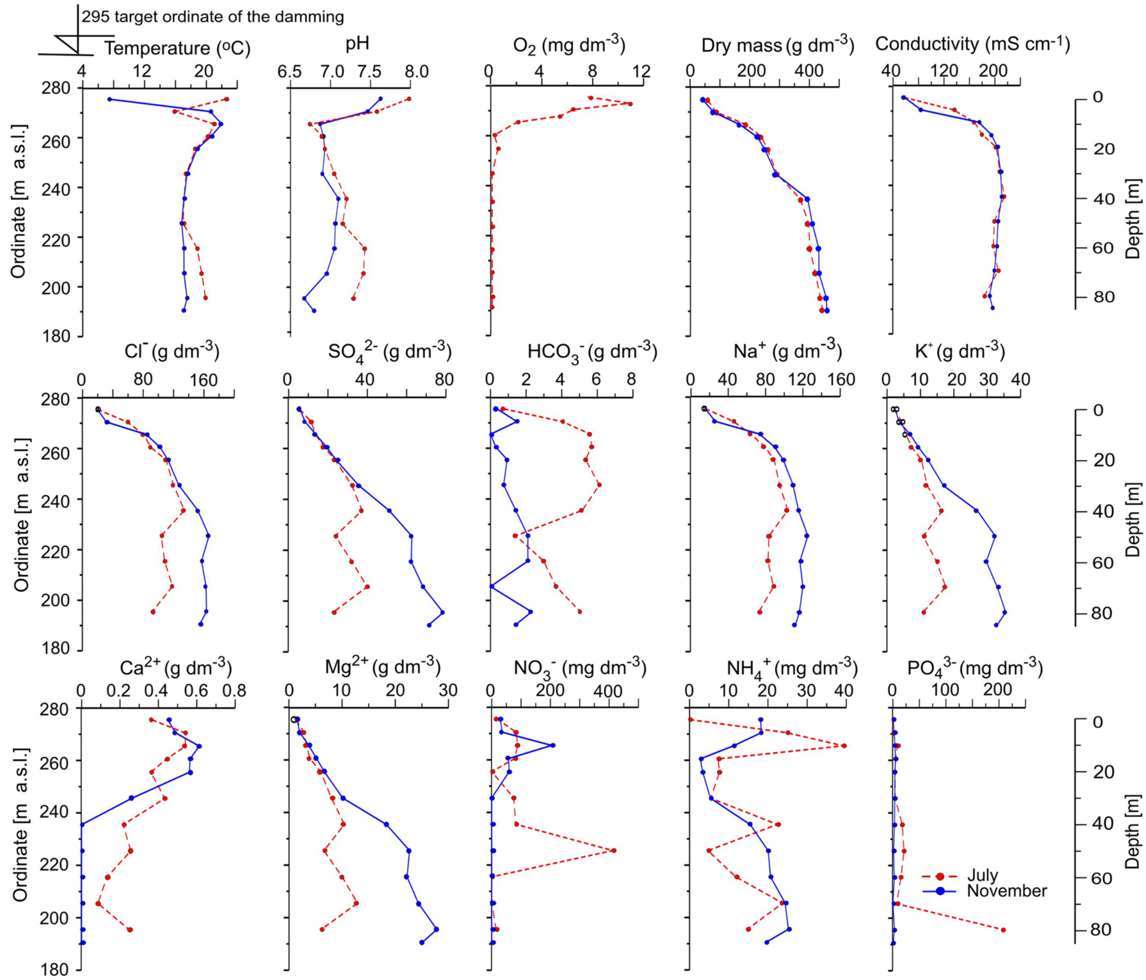


Fig. 3 Values of physicochemical parameters in the water of the Dombrovska pit lake in July and November 2015

Table 1 The significance of differences between the values of the physicochemical parameters in the water of Dombrovska pit lake between July and November 2015 (Wilcoxon test)

Parameter	N	Z	p	Months
pH	10	2.19	0.028	July > November
Cl^-	11	2.31	0.021	November > July
SO_4^{2-}	11	2.49	0.013	November > July
HCO_3^-	9	2.43	0.015	July > November
Na^+	11	2.31	0.021	November > July
K^+	11	2.76	0.006	November > July
Mg^{2+}	11	2.58	0.010	November > July
PO_4^{3-}	8	2.52	0.012	July > November
Cd	11	2.67	0.008	November > July
Cu	11	2.76	0.006	November > July
Zn	11	2.93	0.003	November > July
Mn	11	2.93	0.003	November > July
Ni	11	2.58	0.010	November > July

Only significant differences are given

p significance level

the depth of 0–30 m, while below 30 m towards the bottom, they were higher in November compared to July. In July, ion concentrations showed a more irregular pattern below a depth of 40 m compared to November. Correlation coefficients between these ions confirm their interrelationship in the water column (Table 2) and their higher concentrations in November than in July (Table 1). Concentrations of Ca^{2+} and HCO_3^- showed considerable variability (Fig. 3). We found a positive correlation between HCO_3^- and Ca^{2+} (Table 2).

The pit lake water was highly mineralized (expressed as dry mass, 44.7–420.0 g dm^{-3}; Fig. 3). Mineralization increased with pit lake depth, reaching its highest values in the near bottom water in July and November, which was seven- and nine-fold higher, respectively, than the surface water. Concentration of dry mass showed a negative correlation with pH and DO and was positively correlated with major anions and cations, especially Cl^- and Na^+, and metals (Table 2).

Table 2 The relationship (Pearson's correlation coefficients) between the physicochemical parameters of water of the Dombrovska pit lake

	pH	D.O.	O_2 sat.	EC	Cl^-	SO_4^{2-}	HCO_3^-	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cd	Pb	Cu	Zn	Mn	Fe	Ni
pH	1.00																	
D.O.	0.67[a]	1.00																
O_2 sat.	0.68[a]	1.00[c]	1.00															
EC	−0.69[c]	−0.93[c]	−0.95[c]	1.00														
Cl^-	−0.66[c]	−0.90[c]	−0.91[c]	0.87[c]	1.00													
SO_4^{2-}	−0.49[a]	−0.77[b]	−0.78[b]	0.59[b]	0.90[c]	1.00												
HCO_3^-	ns	ns	ns	ns	ns	ns	1.00											
Na^+	−0.72[c]	−0.92[c]	−0.93[c]	0.91[c]	0.99[c]	0.83[c]	ns	1.00										
K^+	−0.48[a]	−0.78[b]	−0.78[b]	0.58[b]	0.90[c]	0.99[c]	ns	0.84[c]	1.00									
Mg^{2+}	−0.45[a]	−0.70[a]	−0.70[a]	0.52[a]	0.87[c]	0.99[c]	ns	0.79[c]	0.99[c]	1.00								
Ca^{2+}	ns	−0.85[c]	−0.86[c]	0.50[a]	0.50[a]	0.56[a]	0.76[c]	ns	0.48[a]	0.54[a]	1.00							
Cd	−0.68[c]	−0.81[b]	−0.84[c]	0.65[c]	0.89[c]	0.88[c]	ns	0.88[c]	0.91[c]	0.88[c]	ns	1.00						
Pb	−0.58[b]	−0.79[b]	−0.81[b]	0.65[c]	0.92[c]	0.95[c]	ns	0.88[c]	0.96[c]	0.94[c]	ns	0.96[c]	1.00					
Cu	−0.55[b]	−0.72[a]	−0.76[b]	0.48[a]	0.81[c]	0.89[c]	ns	0.77[c]	0.92[c]	0.91[c]	ns	0.97[c]	0.94[c]	1.00				
Zn	ns	−0.80[b]	−0.81[b]	0.46[a]	0.77[c]	0.82[c]	ns	0.73[c]	0.87[c]	0.85[c]	ns	0.89[c]	0.87[c]	0.93[c]	1.00			
Mn	−0.53[b]	ns	ns	ns	0.77[c]	0.90[c]	ns	0.71[c]	0.92[c]	0.92[c]	ns	0.93[c]	0.92[c]	0.98[c]	0.90[c]	1.00		
Fe	−0.47[b]	ns	ns	0.50[a]	0.76[c]	0.87[c]	ns	0.68[c]	0.86[c]	0.86[c]	ns	0.76[c]	0.83[c]	0.76[c]	0.65[c]	0.79[c]	1.00	
Ni	−0.66[c]	−0.71[a]	−0.73[a]	0.61[b]	0.89[c]	0.90[c]	ns	0.86[c]	0.93[c]	0.91[c]	ns	0.99[c]	0.97[c]	0.97[c]	0.89[c]	0.95[c]	0.77[c]	1.00
Dry mass	−0.58[b]	−0.93[c]	−0.94[c]	0.86[c]	0.96[c]	0.88[c]	ns	0.92[c]	0.86[c]	0.84[c]	0.74[c]	0.76[c]	0.84[c]	0.67[c]	0.66[c]	0.66[c]	0.76[c]	0.77[c]

D.O. dissolved oxygen, *EC* electrical conductivity, *ns* not significant

[a]$p \le 0.05$, [b]$p \le 0.01$, [c]$p \le 0.001$

Concentrations of nutrients in the pit lake water were high (nd–413 mg dm^{-3} for NO_3^-, nd–39.3 mg dm^{-3} NH_4^+ and nd–210.6 mg dm^{-3} PO_4^{3-}). Nutrients showed vertical variation (Fig. 3), lower nitrate concentrations were found in deep waters and the highest concentrations were at depths of 50 m in July and 15 m in November. The NH_4^+ levels showed an irregular vertical pattern in July, with the highest value at 15 m and the lowest values at the surface and at 50 m. In November, NH_4^+ levels increased from a depth of 15 m towards the bottom. Phosphates concentrations were greater in deeper water, with the peak concentration in the near-bottom water in July. Phosphate concentrations was higher in July than in November (Table 1). Nutrient concentrations were not correlated with other physicochemical parameters.

Metals

The metal concentrations in the lake water were in the following ranges: 148–1485 μg dm^{-3} for Cd, 0.4–7.3 mg dm^{-3} for Pb, 79–760 μg dm^{-3} for Cu, 99–2040 μg dm^{-3} for Zn, 1.7–11.0 mg dm^{-3} for Mn, 0.4–5.9 mg dm^{-3} for Fe, and 0.4–4.0 mg dm^{-3} for Ni. Metal concentrations were lower in the surface water in July and at depths of 0–5 m in November (Fig. 4). In the deeper layers, metal concentrations (with the exception of Fe) were rather similar in July, but gradually increased in November. The concentrations of Cd, Pb, Cu, and Ni showed little variability from a depth of 50 m towards the bottom. Most metals decreased in the near-bottom water.

Metal concentrations were negatively correlated with pH (with the exception of Zn), DO, and oxygen saturation (with the exception of Mn and Fe; Table 2) and positively correlated with Cl^-, SO_4^{2-}, Na^+, K^+, and Mg^{2+}. The strongest correlations were between Cd, Pb, Cu, Ni, Cl^-, and SO_4^{2-} and between Fe and Mn and Cl^- and SO_4^{2-}. The concentrations of Cd, Cu, Zn, Mn, and Ni were higher in November than in May (Table 1).

Hydrocarbons

We only found trace amounts of hydrocarbons, with no major peaks in the range of the light hydrocarbons < nC10. The retention was analysed for the range defined by the boiling point of n-paraffinic hydrocarbons nC10–nC36. Within this range, three peaks with a retention time characteristic of C21, C26, and C29 appeared in a sample from a depth of 85 m. The sample from 50 m showed a peak of an

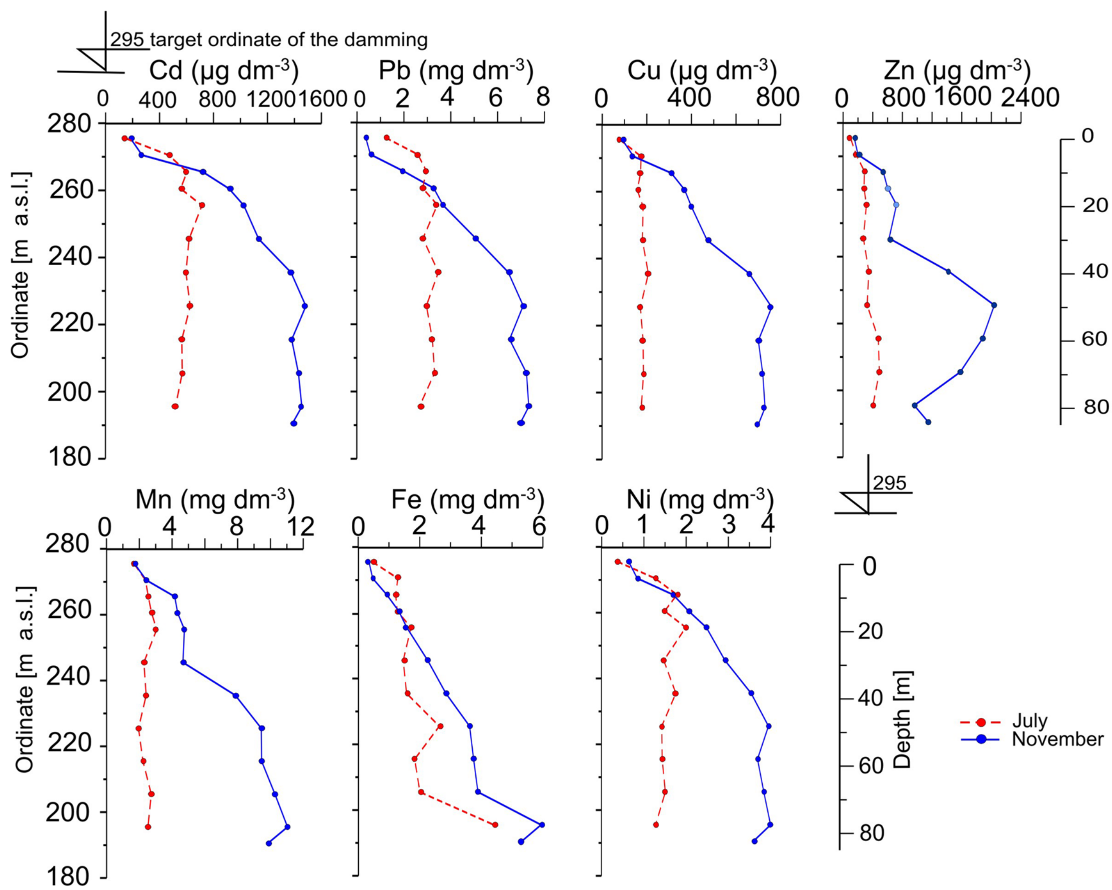


Fig. 4 Concentrations of heavy metals in the water of the Dombrovska pit lake in July and November 2015

unidentified hydrocarbon between a retention time of C11 and C12. Subsequent peaks were assigned to C15 and C21, while an unidentified hydrocarbon had a retention time typical of C23 and C24 (Fig. 5, left-hand graph).

The boiling point of the substance was close to that of n-paraffinic hydrocarbons (Fig. 5). Other alkanes were present, albeit in small amounts. The concentration of alkane (paraffin) hydrocarbons was low, <0.1 mg dm^{-3} near the bottom (85 m) and higher, 0.2 mg dm^{-3} at a depth of 50 m.

Biota

In the non-preserved samples, we observed a rich population of small nanoplanktonic heterotrophic flagellates, with a diameter of about 2 µm, and unicellular algae. Analysis of chlorophyll concentrations confirmed the presence of algae from various systematic taxa (Table 3). Chlorophylls were present in low concentrations throughout the lake beyond the light transmission range. Besides flagellates, live ciliates and one rotifer species were observed. Single aphids and Acarina were found. Among autotrophic seston organisms, some Bacillariophyta and *Ceratium* sp. were noted, as well as plant tracheas and their pollens. In June, we registered the live rotifer *Brachionus plicatilis* and two species of ciliates, *Paradileptus elephantinus* and *Tindinnidium* sp. In addition to the living organisms, we found a few dead rotifers, cladocerans and copepods, 19 species in total (Table 4). In autumn, the only live species was *B. plicatilis*, and Protozoa were absent. Including dead organisms, we noted a total of 10 species (Table 5).

The occurrence of *Tintinnidium* sp. was limited to the euphotic zone (to a depth of 2.5 m). *Paradileptus elephantinus* was most numerous at a depth of 5 m and penetrated the water layer up to a depth of 40 m into anoxic environments.

Table 3 Vertical distribution of chlorophyll concentration in the Dombrovska pit lake

Depth m	Chl. *a* µg dm^{-3}	Chl. *b* µg dm^{-3}	Chl. *c* µg dm^{-3}
0	0.74	7.82	1.16
2.5	0.56	5.50	1.25
5	2.95	9.18	3.91
15	0.85	5.66	1.68
30	4.40	20.31	15.94
70	1.67	11.28	1.63

Brachionus plicatilis was observed throughout the water profile with a maximum density at a depth of 7.5 m in June. In autumn, *B. plicatilis* was observed in the upper 20 m layer with a maximum density at a depth of 20 m (Tables 4, 5).

The analysed benthic sample comprised several diatom taxa that are known to occur in inland saline spring water (Wojtal 2013) and other athalassic habitats (Żelazna-Wieczorek et al. 2015). The material was dominated by *Nitzschia pusilla* and some *Halamphora* species (*H. borealis, H. tenerrima, H acutiuscula*). We also identified *Navicula cincta, N. phylleptostoma, N. salinicola, Navicymbella pusilla, Nitzschia epithemoides, N. hungarica, N. scalpeliformis*, and *Staurophora lanceolata*.

Discussion

According to the classification of mine water quality (Pluta and Grmela 2006), the upper layer (surface 5–10 cm in May, and 0–5 m in November) of the pit lake was classified as moderately saline, and the deeper layer as brine.

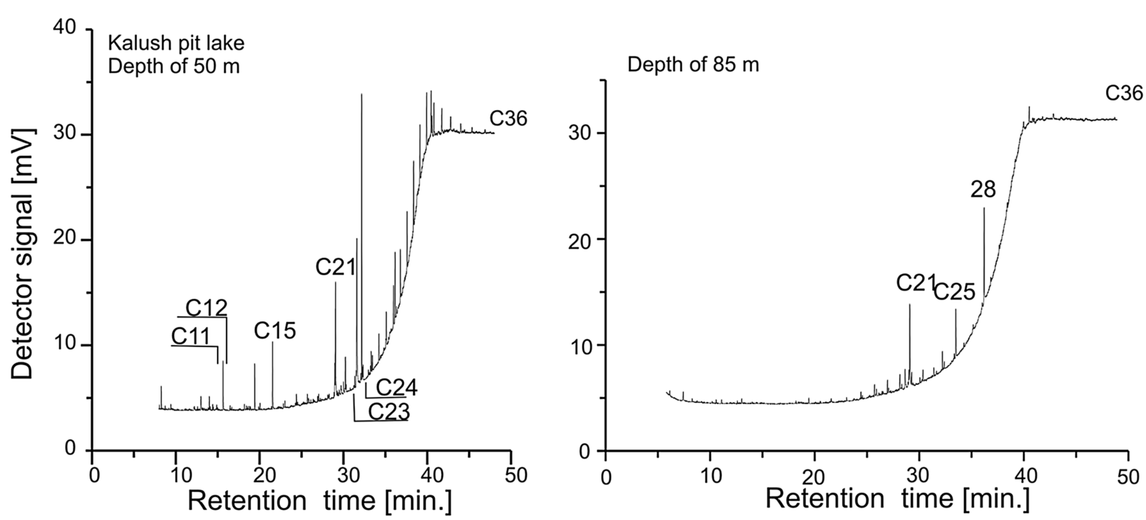


Fig. 5 Chromatograms of alkanes C10–C40 from the depths of 50 and 85 m of the Dombrovska pit lake

Table 4 Zooplankton densities in the vertical profile of the Dombrovska pit lake in July, individuals/L (transparency 2 m)

Taxon	Depth (m)												
	0	2.5	5	7.5	10	15	40	30	40	50	60	70	83
Ciliata													
Paradileptus elephantinus	2.5	2.9	29.4	6.4	5	6.6	6.6		0.5				
Tintinidium sp.	+	+											
Rotifera													
Brachionus plicatilis	3	5.8	53.4	34.1	13.6	2.3	2	7.0	5.8	4.6	1.8		0.2
B. angularis					0.3								
B. diversicornis							0.2						
Cephalodella sp.					0.3								
Filinia opoliensis					0.3								
F. limnetica					0.3								
F. longiseta					0.7	0.4	0.6			0.4		0.4	
Keratella quadrata		0.4	1.8	4.26	3.1	3.9	12.6	9.1	5.3	3.6	1.8	0.8	
K. cochlearis		0.2	0.6		0.7	3.1	8.4	1.2	3.9	1.1	1.1		
K. testudo							2.4	0.4					
Lepadella ovalis			0.6		0.3								
Trichocerca sp.						0.8							
Cladocera													
Alona rectangula										0.4			
Bosmina longirostris				1.1			1.6	2.0	1.9	0.7	1.1		0.2
Chydorus sp.				1.1									
Ceriodaphnia sp.										0.7	0.4		
Copepoda													
Thermocyclops crassus							0.2				0.4		
Copepoda non det												0.2	
Nematoda													
Nematoda non det.										0.4			
Sum of zooplankton	5.5	9.3	85.8	46.9	24.6	17.1	34.6	19.7	17.4	11.9	6.6	1.4	0.4
Without *P. elephantinus*	3.0	6.4	56.4	40.5	19.6	10.5	28.0	19.7	16.9	11.9	6.6	1.4	0.4

Table 5 Zooplankton densities (individuals dm^{-3}) in the vertical profile of the Dombrovska pit lake in November, (transparency 8 m)

Taxon	Depth (m)										
	0	2.5	5	10	20	30	40	50	60	70	80
Rotifera											
Brachionus plicatilis live	0.45	1.45	0.35	0.05	3						
B. calyciflorus						0.05					
Keratella cochlearis	0.05	0.05	0.05	0.05	0.05			0.05			
K. tecta		0.05	0	0							
K. quadrata	0.3	0.45	0.05	0.3	0.1	0.15		0.05			
Lecane monostyla		0.05									
Cladocera											
Daphnia longispina	0.05										
Alona sp.					0.05						
Bosmina longirostris		0.05				0.05	0.05	0.05			
Copepoda											
Copepoda non det.						0.05					
Acarina	0.05										

Moderately saline water is characterized by a dry residue ranging from 3 to 70 g dm^{-3} and concentrations of Cl^- and SO_4^{2-} from 1.8 to 42 g dm^{-3}, while brine is characterized by a dry residue > 70 g dm^{-3} and concentrations of Cl^- and SO_4^{2-} > 42 g dm^{-3} (Pluta and Grmela 2006). For biological purposes, Hammer's classification is often used. According to Hammer (1993), the surface 5–10 cm layer belongs to the mesohaline type (20–50 g dm^{-3}), whereas the lower layer is hypersaline sensu Hammer, > 50 g dm^{-3}. The concentrations of anions and cations (with the exception of Ca^{2+}) in the brine greatly exceeded the concentrations in sea water (Kabata-Pendias and Pendias 1999). The high levels of Na–Cl in the brine is presumably due to dissolution of halite from the slopes. The Cl^- concentrations in the lake are similar to those in highly mineralized water bodies such as the Dead Sea, which has the characteristics of Ca–Cl brine (Gavrieli et al. 2001). The meromixis of the studied pit lake is classified as ectogenic, in contrast to biogenic and crenogenic meromixis (Boehrer and Schulze 2006).

Analysis of the pit lake's chemistry shows the formation of two layers with different levels of mineralization and a seasonal increase in the mesohaline layer. Although the final salinity of the upper layer, when the lake chemistry stabilizes after the pit fills in 2025, is still unknown, we found it to be less mineralized (44.7 g dm^{-3} in November) than predicted by Dolin et al. (2010). Our results align more with Gajdin et al. (2014) and Gaydin and Diakiv (2010), who predicted the ultimate occurrence of a freshwater surface layer. We observed decreasing salinity, from 179.1 to 44.7 g dm^{-3}, from a depth of 10 m to the near-surface in November, indicating a diminishing rate of salinity with decreasing depth of 13.4 g dm^{-3} m^{-1}. Using the linear rate of salinity decrease, we predict that the pit lake may have layer of freshwater containing ≈ 1 g dm^{-3} of dry residue at an elevation of 279 m a.s.l. (i.e. 4 m above the current lake level, with the pit filling at a rate of about 4 m per year). However, confirmation of our prognosis requires future validation.

Lakes like Lake Mogilnoe on Kildin Island in the Barents Sea (Fokin et al. 2004; Strelkov et al. 2014) and the Big

Table 6 Examples of the prevalence of zooplanktonic species in the waters of varying salinity

Species	Salinity (g dm^{-3})	References
Acanthocyclops sp.	210	Anufriieva et al. (2014)
Diacyclops bisetosus and *Cyclops furcifer*	140–150	Anufriieva et al. (2014)
Eucyclops sp.	150	Anufriieva et al. (2014)
Acanthocyclops robustus	< 20	Brucet et al. (2009)
Eurytemora velox	< 45	Brucet et al. (2009)
Calanipeda aquaedulcis	< 40	Brucet et al. (2009)
Eucyclops serrulatus	< 55	Brucet et al. (2009)
Cletocamptus confluens, Apocyclops cf. *dengizicus*	100–240	Carrasco and Perissinotto (2012)
Ciliate *Fabrea* cf. *salina*	100–240	Carrasco and Perissinotto (2012)
Hexarthra fennica, Brachionus plicatilis	< 49.89	Del Ponti et al. (2015)
Boeckella poopoensis, Cletocampthus deitersi	< 49.89	Del Ponti et al. (2015)
Metacyclops mendocinus; Brachionus angularis	< 15.8	Del Ponti et al. (2015)
B. dimidiatus; Keratella tropica, K. cochlearis, Synchaeta sp.	< 15.8	Del Ponti et al. (2015)
Oithona nana, Centropages ponticus	39–45	Gilabert (2001)
Acartia spp. (mainly latisetosa)	39–45	Gilabert (2001)
Asplancha girodi	3–111	Hammer (1993)
Brachionus plicatilis	13–146	Hammer (1993)
Keratella quadrata	2.8–103	Hammer (1993)
Artemia franciscana	33–269	Hammer (1993)
Daphnia similis	3–104	Hammer (1993)
D. connexus	9–82	Hammer (1993)
Diacyclops thomasi	3–72	Hammer (1993)
Hexarthra fennica	< 100 and pH > 9.2	Hammer (1993)
Moina hutchinsoni	< 100 and pH > 9.2	Hammer (1993)
Hexarthra polyodonta	< 100 and pH > 9.2	Hammer (1993)
Cletocamptus albuquerquensis	17–126	Hammer (1994)
Keratella cochlearis	< 25	Hammer (1994)
Boeckella poopoensis	1–90	Rios and Crespo (2004)

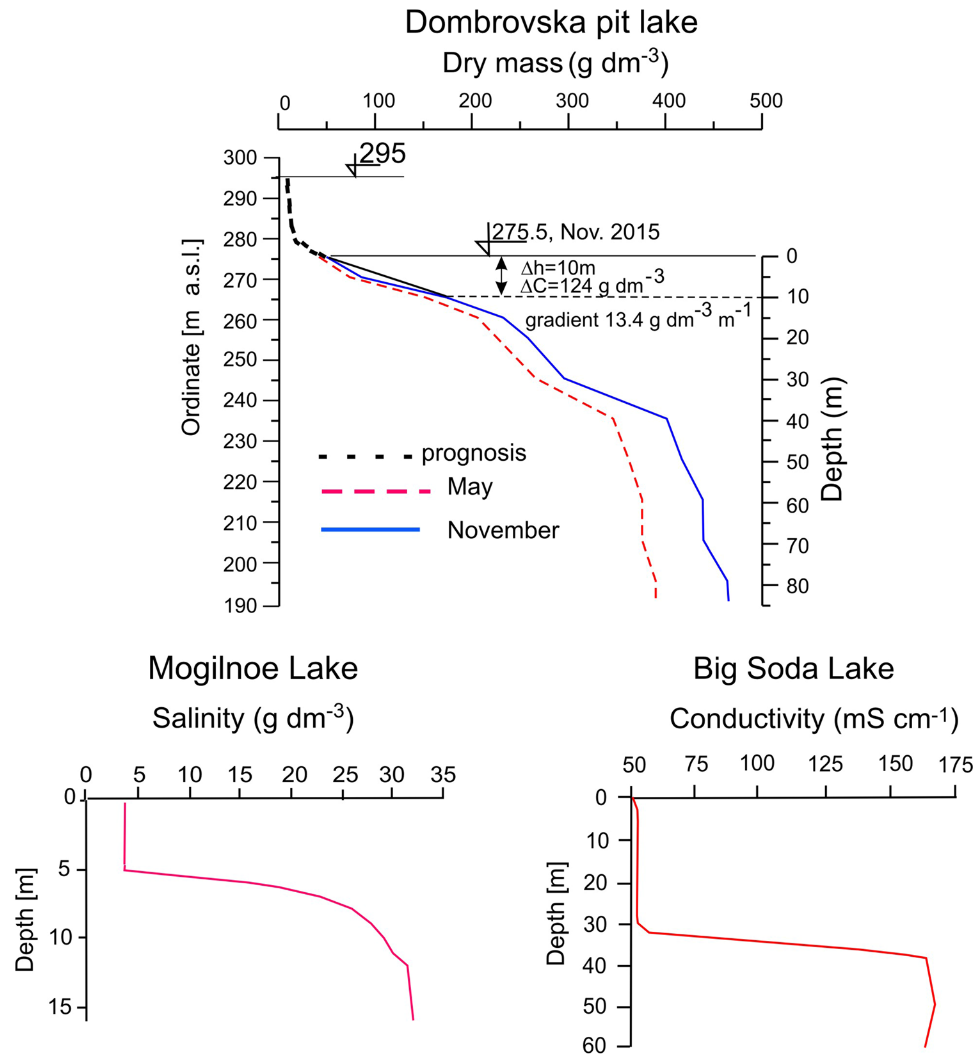


Fig. 6 Trend of desalinization of the Dombrovska pit lake in May and November 2015 and two stable layers in the Big Soda Lake (Cloern et al. 1983) and the Mogilnoe Lake (Fokin et al. 2004) for comparison; abbreviations: Δ h—depth difference, Δ C—difference in salinity concentration between 0 and 10 m

Soda Lake in the USA (Cloern et al. 1983) (Fig. 6), demonstrate that surface water layers may not have a salinity <3 g dm^{-3}, but may instead be hyposaline sensu Hammer (1993; 3–20 g dm^{-3}). The Mogilnoe Lake on Kildin Island on the Kola Peninsula in Russia was created as a separate bay of the Barents Sea about 1000 years ago. Currently, it has a depth of 17 m and is separated from the sea by a 3.7–5.4 m natural dike with a width of 63–70 m. The Mogilnoe Lake is hyposaline sensu Hammer (1993) in the surface layer and saline below. Another example is the the Kislo-Sladkoe Lake (Krasnowa and Pantyulin 2013; Krasnowa et al. 2014), which has layers of fresh, brackish (1000–4000 g dm^{-3}), and salty water with hydrogen sulphide.

In the Dombrovska pit lake, the similarity in the vertical distribution of Cl^-, SO_4^{2-}, Na^+, K^+, Mg^{2+}, and metals may indicate similar mineralogical (or geological) sources and geochemical pathways for metals and ions. Some irregularities in the Cl^-, SO_4^{2-}, Na^+, K^+, Mg^{2+} concentrations in brine in the Dombrovska pit lake may be related to biogeochemical processes in the water column, chemical composition of groundwater supplying the pit lake, leaching of elements from easily soluble salts created by slopes and/or mixing of water. The Dombrovska pit lake is not yet completely filled with water; therefore, the freshwater inflow and mixing of freshwater and brine may still further modify water quality and the spatial distribution of elements in the water column. As the banks/slopes of the opencast had not been covered by any material before filling with water, minerals are continuously leached, this may lead to an increase in the concentration of some ions at certain depths.

The Dombrovska pit water is heavily contaminated. Concentrations of Fe are an order of magnitude greater, Cu, Zn, Mn, and Ni two orders of magnitude greater, and Cd and Pb three orders of magnitude greater than those found in less polluted water (Karnaukhova 2008; Szarek-Gwiazda and Mazurkiewicz-Boroń 2006). The Pearson's correlation indicates that the geochemical pathway of metals in the lake water is affected by inorganic ligands (chlorides and sulphides). The ligands keep the metals in solution and influence their vertical variation. Interdependency of metals with strong inorganic ligands is often observed in meromictic lakes (Szarek-Gwiazda and Żurek 2006; Taillefert and Gaillard 2002).

The decreased concentrations of Cd, Pb, Zn, Mn, and Ni, and SO_4^{2-} in the near-bottom water is probably due to sulphate reduction and precipitation of metal sulphides. This has been observed in other meromictic reservoirs and lakes (Balistrieri et al. 1994; Szarek-Gwiazda and Żurek 2006). Inversely, increased concentrations of Fe and PO_4^{3-} in the near-bottom water of the Dombrovska pit lake in July indicate their release from the sediment. The amount of Fe and phosphorus released from the sediment and interstitial water to the near-bottom water depends on both Eh and pH. At neutral pH, the solubility of $FePO_4$ is about 450 mg dm^{-3} and increases at a pH > 7.5 (Golubiev and Savenko 2002). Measured Fe and phosphate concentrations did not exceed the oversaturation threshold for $FePO_4$ precipitation. Hydrous Fe and Mn oxides are important scavengers of metals in various aquatic ecosystems; therefore, metal distribution in the water column of lakes and reservoirs is often related to Fe cycling (Szarek-Gwiazda and Żurek 2006; Taillefert and Gaillard 2002). Positive correlations between Mn, Fe, Cd, Pb, Cu, Zn, and Ni indicate that Fe and Mn oxides/hydroxides play an important role in the geochemical pathway of other metals in the lake.

The Dombrovska pit lake has a thermal profile totally different from those of other freshwater lakes. The temperature of the less mineralized water (depth 0–5 m) changes seasonally and is higher in July than in November. In July, because the period of high air temperatures is relatively short and the surface water absorbs most of the solar radiation, the temperature varies from about 22 °C at the surface to 16 °C at a depth of 5 m. From a depth of about 10 m to the bottom, there is no seasonal variation in temperature, which was found to be almost a constant (18 °C), despite an air temperature of less than 0 °C in November. Because brine is denser than the upper brackish water, the warm water does not rise. This phenomenon was also observed in the hypersaline, permanently ice-covered Vanda Lake (depth 68 m) in the Antarctic (Wilson and Wellman 1962). There, the ice cover had a thickness of 3.5 m and the air temperature was − 40 °C. The temperature of Vanda Lake water was 19.2 °C at a depth of 57.5 m. This "anomaly" is a result of heat trapped in saline lakes, which act as solar collectors. A detailed description of this heat trap mechanism and the physical processes of a solar pond are given by Hull (1979) and Weinberger (1964).

The low concentrations of hydrocarbons found at depths of 50 and 83 m may be explained in two ways: hydrocarbons released from included oil fluid in salt minerals, and pollution, possibly due to ore exploitation and transport. Light fractions of anthropogenic hydrocarbons evaporate or float up during flooding, and heavy fractions concentrate at the bottom or are gravitationally fractionated, depending on their density. Since the clay minerals at the pit base (50–83 m) contain heavy hydrocarbon fractions, the anthropogenic origin of the hydrocarbons is more probable.

In the shallow mesohaline water layer, only three live species were found: the rotifer *Brachionus plicatilis* and two Ciliata taxa: *Paradileptus elephantinus* and *Tindinnidium* sp. Such high salt concentrations can be toxic for water organisms (Cowgill and Milazzo 1990; Kipriyanova et al. 2007). Most macroinvertebrates are able to live at salinity levels < 2 g dm^{-3}, but for some macroinvertebrates, the salinity threshold is below 1 g dm^{-3}. In nature, increased salinity levels between 1 and 5 g dm^{-3} cause a reduction in both species richness and abundance of zooplankton. Similar results were found by Kipriyanova et al. (2007) who noticed a decrease in species richness of zooplankton from 61 to 16 species as salinity increased from 0.8 to 6.4 g dm^{-3}. The hatching of resting eggs was inhibited at higher salinity levels between 16 and 32 g dm^{-3}. However, some resting eggs remained viable and hatched when being returned to freshwater (Santangelo et al. 2014). Also, KCl is much more toxic than NaCl or CaCl to zooplankton and fish (Doudoroff and Katz 1953).

Experimental data show that acute toxicity (as LC50) for freshwater cladocerans occurred below 3 g dm^{-3} of NaCl; however, for *Daphnia magna*, toxicity was observed at various concentrations: 6.7 g dm^{-3} by Cowgill and Milazzo (1990), 3.68 g dm^{-3} by Anderson et al. (1948), and 4.625 g dm^{-3} by Biesinger and Christensen (1972). The 96 h LC50 for caddisfly, mayfly, and midge ranged between 3.5 and 6 g dm^{-3}; other mayfly species are usually more sensitive (< 0.7 g dm^{-3}). Anderson et al. (1948) reported a 64 h immobilisation threshold for *Cyclops vernalis, Mesocyclops leuckartii, Diaptomus oregonensis, Leptodora kindti*, and *D. magna* in the range of 0.127–0.640 g dm^{-3} of KCl and 3.030–6.100 g dm^{-3} of NaCl. However, laboratory toxicity tests results are often inconsistent with field observations. For example, Anufriieva et al. (2014) evaluated hypersaline water bodies from the Crimean Peninsula and reported four Copepoda: *Acanthocyclops* sp. at a salinity of 210 g dm^{-3}; *Eucyclops* sp. copepodit at 150 g dm^{-3}; *Diacyclops bisetosus* and *Cyclops furcifer* at 140–150 g dm^{-3} (Table 6). It is likely that some freshwater species are able to adapt to higher salinity levels in natural environments.

The occurrence of *Paradileptus elephantinus* and *Tindinnidium* sp. in the deeper hypersaline layer of the Dombrovska pit lake were unexpected (Table 5). We therefore considered that these species had adapted to the hypersaline water or sank from the upper layer into deeper layers, if sinking is possible in this dense hypersaline water. The specific density (measured aerometrically) of the pit lake water is high, from 1.032 g cm^{-3} at the surface to 1.113 g cm^{-3} at a depth of 10 m and to 1.282 g cm^{-3} in the near-bottom water (85 m) (unpublished data). The specific gravity of chitin is between 1.39 and 1.41 g cm^{-3} (Sollas 1907). Therefore sinking of chitin in the salt water is possible. The dead planktonic animals we observed were probably washed in from surrounding freshwater bodies and died of osmotic shock on contact with the saline pit lake water. In this sense, this saline lake might be a trap for freshwater animals.

Samples of the lake water were rich in diatoms and had a similar taxa composition as other saline springs (Wojtal 2013; Żelazna-Wieczorek et al. 2015). The diatoms found have also been observed in water with very high EC values and with high amounts of calcium, magnesium, and other cations (Wojtal 2013). Diatoms can inhabit waters with extremely low oxygen levels. Several taxa are exclusive to oxygen-poor water (e.g. *Halamphora borealis, H. tenerrima, H. acutiuscula, Navicula phylleptostoma, N. salinicola*, or *Staurophora lanceolata*), which is related to their ability to inhabit highly saline inland waters. Moreover, *Halamphora tenerrima* is known from marine environments (Żelazna-Wieczorek et al. 2015). Species such as *Navicula cincta, Navicymbula pusilla, Nitzschia hungarica*, and *N. pusilla* are widely distributed in waters rich in dissolved minerals (Krammer and Lange-Bertalot 1986, 1988; Wojtal 2013; Żelazna-Wieczorek et al. 2015), including those rich in metal ions. The diatoms, which have rarely been reported in water with high EC levels, were also relatively rare species here.

Conclusions

The high mineralization of the ectogenic Dombrovska pit lake water creates a remarkable aquatic environment. The pit lake is not yet completely filled with water and the water quality has not reached its final state, due to the inflow and mixing of freshwater and brine. In contrast to typical meromictic lakes, which are usually divided into three layers (mixolimnion, monimolimnion, and chemocline), the Dombrovska pit lake has only two distinct layers: a thick (ca. 10 m) upper mesohaline, oxic layer, and a large (ca. 75 m) anoxic hypersaline layer (monimolimnion), rich in major anions and cations (except for Ca^{2+}), metals, and nutrients. The two layers do not mix and in this sense, the Dombrovska pit lake is fairly unique. The directions of changes in water chemistry tend to confirm our hypothesis that, after fully filling the void, the pit lake will have a freshwater or brackish water upper layer and a lower, saline monimolimnion. The change from present lake status to the meromictic lake type is predicted and will involve the gradual increase in thickness of the upper, oxic (mixolimnion) layer. The deep lower, anoxic layer, rich in ions and metals will remain but will be less thick. We were unable, based on current data, to predict the final salinity of the upper layer, whether it will be fresh or brackish water. We predict that in the future, a "true" meromic pit lake with classical chemical stratification in the water column will be formed. However, our prognosis requires verification in further studies.

High water mineralization and concentrations of metals creates unsuitable conditions for most biota. In terms of zooplankton, only three living taxa were found: the rotifer *Brachionus plicatilis* and two species of ciliates, *Paradileptus elephantinus* and *Tindinnidium*. In the littoral part of the pit lake, we found diatoms resistant to high salinity, such as *Nitzschia pusilla* and some *Halamphora* species (*H. borealis, H. tenerrima*, and *H. acutiuscula*). Most freshwater species live in waters with a salinity of 1 g dm^{-3} or a little more. With increasing salinity, brackish water species appear. The conspicuous feature of the diatom assemblage is the lack of a widespread, non-saline taxa. As the concentration of ions decreases, taxa with a wide spectrum of tolerance for environmental conditions may appear. As the lake is young and still filling, its chemistry and succession of living organisms are expected to be subject to considerable fluctuations, and additional investigations.

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