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Pit Lakes Affected by a River Contaminated with Brines Originated from the Coal Mining Industry: Evolution of Water Chemistry in the Zakrzówek Horst Area (Krakow, Southern Poland)

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Abstract: Long-term coal mining activities in the Upper Silesia significantly affect the environment in southern Poland. Discharges of brines (with TDS reaching over 110 g/L) from mines are the main source of pollution of many rivers in Poland, including the Vistula River. The Zakrzówek horst is a small geological structure composed of the Upper Jurassic limestones. These limestones were exploited in several quarries. In the largest one (the "Zakrzówek" quarry), exploitation reached the depth of 36 m below the water table, i.e., about 32 m below the average water level in Vistula River which flows 700 m from the quarry. An important part of this inflow into quarries came from the contaminated Vistula River, with a chloride concentration over 2 g/L. The exploitation ceased in 1991, and dewatering ended in 1992. In the old quarry area, pit lakes appeared, which are unique because they present an example of a post-mining site affected by the riverine water contaminated with brines. Investigations of physicochemical parameters of water in the Zakrzówek area were carried out in the period of 1990–2020. Results showed that the largest pit lake was initially meromictic with a distinct stratification. After several years, holomictic conditions developed due to the surface layer freshening and convective mixing.

Keywords: coal mining brines; pit lakes; water chemistry; limestone quarry; Upper Jurassic limestones

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Citation: Motyka, J.; d'Obyrn, K.; Sracek, O.; Postawa, A.; Źróbek, M. Pit Lakes Affected by a River Contaminated with Brines Originated from the Coal Mining Industry: Evolution of Water Chemistry in the Zakrzówek Horst Area (Krakow, Southern Poland). *Energies* **2022**, *15*, 4382. https://doi.org/10.3390/en15124382

Academic Editor: Nikolaos Koukouzas

Received: 24 May 2022
Accepted: 14 June 2022
Published: 16 June 2022

1. Introduction

The term 'pit lake' is commonly used for lakes formed by the flooding of excavated mining pits [1]. Several studies published in the past were focused on pit lakes and formation of acid mine drainage (AMD) waters, i.e., waters with low pH and high concentrations of sulfate and metal(loids) [2–7]. The impact of water chemistry in the pit lakes on aquatic biota has also been studied (e.g., [8,9]). Pit lake wall mineralogy plays an important role in pit lake water chemistry formation, and the interaction with the carbonate pit lake wall may result in complete AMD neutralization [2,10]; however, other factors such as pit lake water balance are also important [11]. In moderate climate conditions, holomictic lakes generally develop, i.e., with mixing of surface and deep waters during spring and fall turnovers. However, meromictic lakes with permanent water chemistry stratification may develop under certain conditions such as the input of organic matter or the accumulation of brines at the pit lake bottom [12,13]. The position of the chemocline in meromictic lakes may change throughout the year [14].

The Zakrzówek horst is a small geological structure located southwest of central Krakow. The exploited part is composed of Upper Jurassic limestones (malm), covered by younger Tertiary and Quaternary sediments. From the 16th to 20th centuries, there was exploitation of limestones and clays for construction purposes [15,16]. In the 1906–1991 period, there was exploitation of limestones in two quarries for the production of soda in Krakow soda factory "Solvay". In the older quarry "Łom na Kapelance", the exploitation of limestone ceased at the end of the Second World War; however, in the younger quarry Zakrzówek, which is much larger and deeper, the exploitation continued from the mid-1950s until 1991, when the Solvay factory was closed. In November 1992, dewatering of the "Zakrzówek" quarry ceased, and controlled flooding began, continuing until July 1997. Since 1996, monitoring of the water chemistry in the "Zakrzówek" quarry has been carried out. In the "Łom na Kapelance" quarry, two shallow reservoirs were formed, and their water chemistry was also monitored.

Objectives of the study were monitoring and interpretation of the water level in deep pit lake PL-1 from 1992 to 1996 and of water chemistry changes in pit lakes PL-1, PL-2, and PL-3, as well as the identification of factors which determine water chemistry evolution in investigated pit lakes after flooding. Generally, mine drainage contaminates surface streams, but it is the other way around in this case. To our knowledge, this is a unique site in the world. Furthermore, we wanted to demonstrate that a meromictic regime could switch to a holomictic regime under the influence of specific conditions.

2. Site Geology and Hydrogeology

In the Zakrzówek area, the exploitation was carried out in numerous small quarries above the water table. In the two largest quarries, the exploitation occurred down to the water table in the quarry "Lom na Kapielance" and even reached a depth of 36 m below the water table in the quarry "Zakrzówek", i.e., about 32 m below the average water level in Vistula River, located 700–900 m away (Figure 1). In the period of "Zakrzówek" exploitation, the quarry was recharged by highly mineralized water from Vistula River contaminated by NaCl brines pumped from the mines in the Upper Silesia Basin located about 80 km from Zakrzówek. Mixing of highly mineralized waters from rivers and fresh groundwaters is relatively rare. In the literature, there are some examples of groundwater mixing with deep mineralized brines or seawater intrusions [17,18]. In Poland, in the Upper Silesia Basin, pits formed by the exploitation of gravels and sands were sometimes used as reservoirs for brines from coalmines. In such pit lakes, vertical stratification of mineralization develops, and the processes of water freshening occur [19].

The Zakrzówek horst is one of numerous horst structures in the Krakow territory, where the Mesozoic rocks are elevated in the surrounding Miocene rocks (Figure 1). The horst is composed of chalky, Upper Jurassic limestones [20–22] and covered by marls and calcareous marls of Upper Cretaceous and Miocene clays which fill karst depressions [23]. The Quaternary sediments are composed of sands, alluvial sediments, and loess. Tectonic faults limiting the Zakrzówek horst from three sides have bearings of NW–SE and NE–SW (Figures 1B and 2).

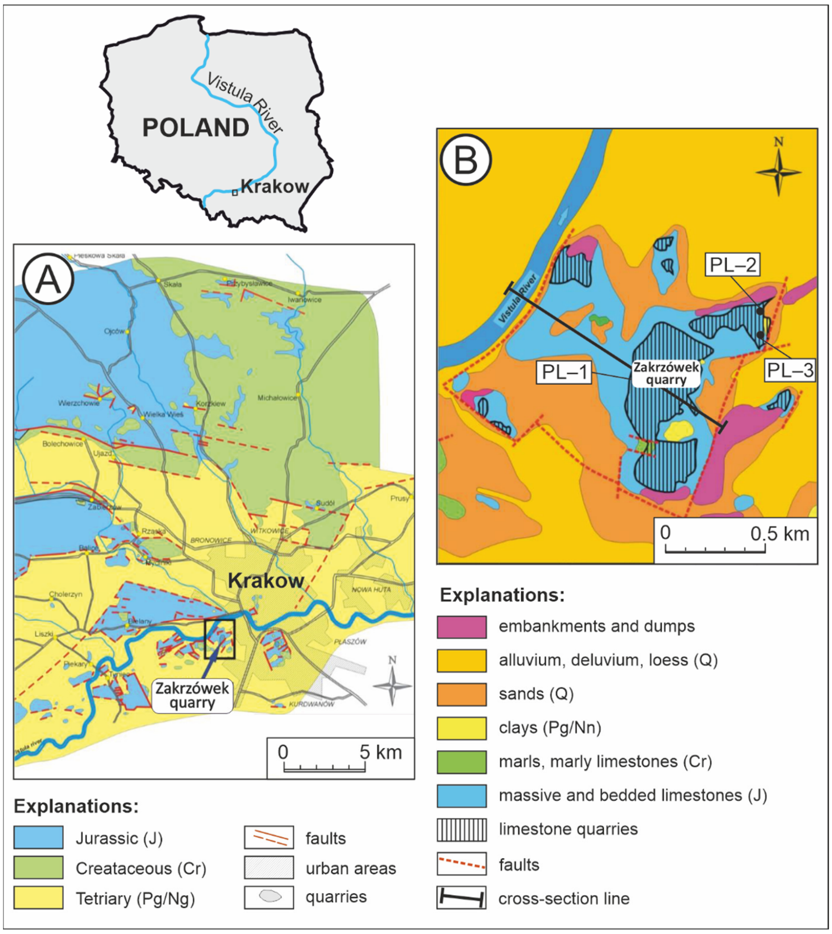


Figure 1. Location and local geology. (**A**). Geological map of Krakow area [24]. (**B**). Geological map of Zakrzówek horst (after [25]). The black line in (**B**) indicates the cross-section presented in Figure 2.

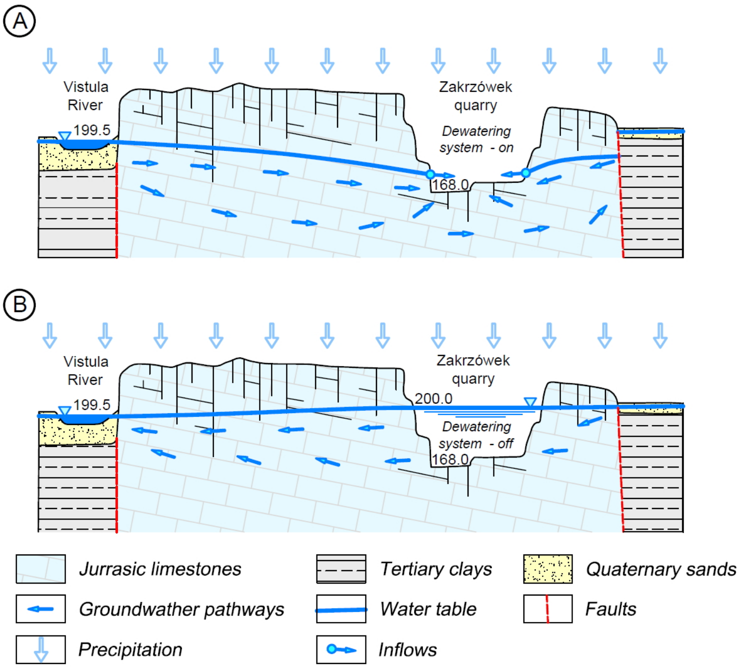
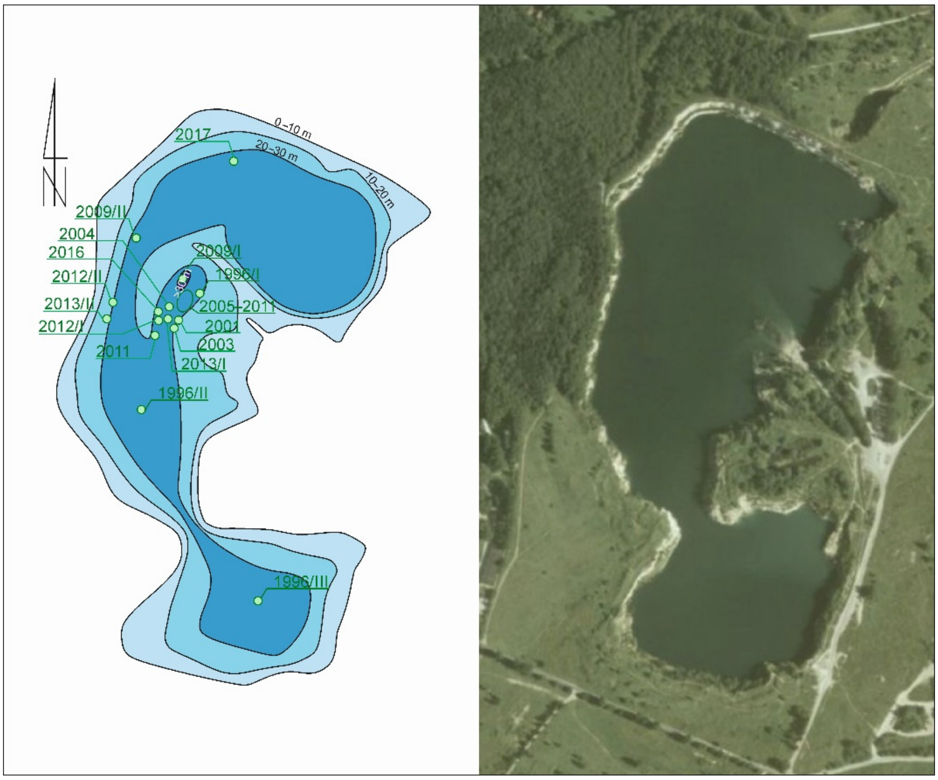


Figure 2. Flow pattern in "Zakrzówek" quarry area. (**A**) Situation during the quarry exploitation. (**B**) Situation after the quarry flooding. The cross-section is shown in Figure 1.

The deep pit lake PL-1 is the largest lake in the Zakrzówek horst (Figure 3). Its surface area A0 is 165,520 m^2, and the length of its shoreline is 2530 m. The shoreline development index D_L [26] is equal to 1.24. Water depth in the central zone is 32 m, and the maximum depth at the former pumping station site reaches 38 m. The relative depth D_R expressed as a percentage [3,27] is equal to 6.79%, which is typical for pit lakes [3].



(**A**) (**B**)

Figure 3. (**A**) Bathymetry of PL-1 based on pre-flooding topography. Sampling points are marked by circles with corresponding sampling dates. (**B**) Satellite image (based on Google Maps).

The main aquifer at the site is associated with Upper Jurassic limestones [25,28]. The limestones form an aquifer of fractured karstic type. This type of aquifer usually shows high heterogeneity of hydrogeological parameters, e.g., a wide range of hydraulic conductivity values. The hydraulic conductivity calculated on the basis of pumping test data from only one well is 3.54×10^{-5} m/s. The hydraulic conductivity of Quaternary sediments is 2.8×10^{-4} m/s [28].

In natural conditions, the Zakrzówek horst with overlying Quaternary sediments was drained by Vistula River in the NW, and the water table followed the local topography. In the late 1950s, the exploitation of limestone in Zakrzówek below the water table level started. The exploitation finished in 1991 at the level of 168 m a.s.l., i.e., 32 m below the average water level in Vistula River (Figure 2A). In November 1992 (18 November 1992), pumping from the quarry ceased and controlled flooding began. The flooding finished in July 1997, i.e., about 4.5 years after cessation of pumping. The process accelerated due to anomalous precipitation in southern Poland in July 1997. Recently, the water level in the flooded quarry was located about 0.5 m above the average water level in Vistula River (Figure 4). Preferential flow along bedding planes and fractures plays an important role and results in flow paths not always following expectations [25].

Water chemistry in the "Zakrzówek" quarry, during the mining stage was formed by atmospheric precipitation, groundwater recharge at Zakrzówek horst, and inflow from Vistula River contaminated by mining NaCl brines with TDS up to 370 g/L [25]. The Cl^- ion is an excellent indicator of the inflow from Vistula River to the quarry. Its concentration in the river depends on the river discharge; in 1990–1993, it was in the range from 62 to 2072 mg/L. Concentration of the ion at different inflow points to the quarry was highly variable, from 50 to 1200 mg/L [29].

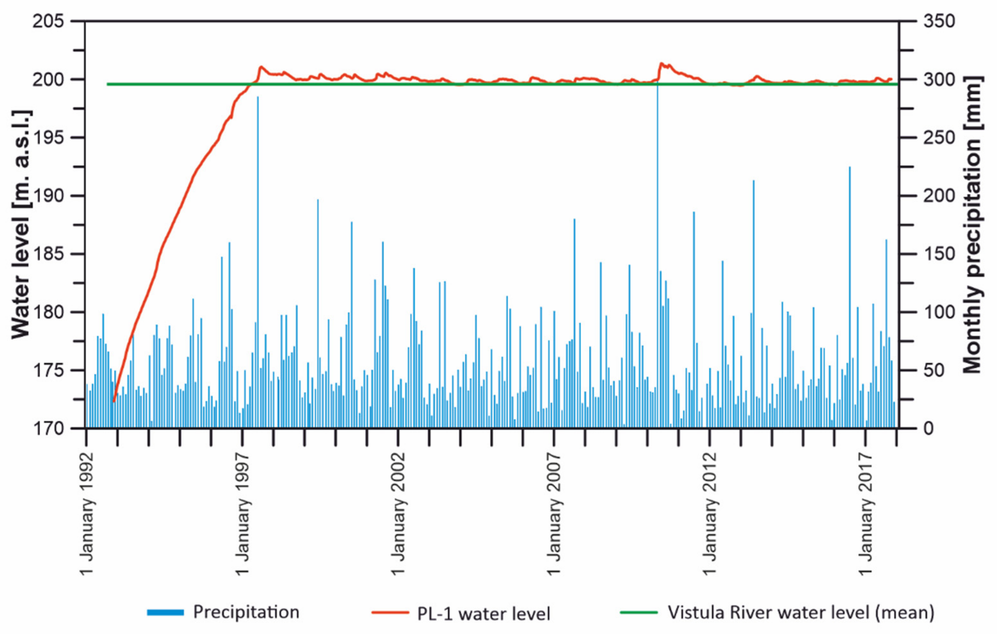


Figure 4. Plot of water level in PL-1 and precipitation from the beginning of flooding (18 November 1992).

3. Materials and Methods

In the "Zakrzówek" quarry, water level was measured from the beginning of flooding in November 1992, initially on adaily basis and, later, when water level was close to equilibrium, on a weekly basis. Monitoring of water chemistry in pit lake PL-1 (Figure 1B) started in winter 1996 when samples were taken at three sites from different depths using the submersible in-line electric pump Whale and analyzed for water chemistry. Monitoring of Cl^- concentration in the surface layer started in July 1998. Samples in complete profiles were collected on an irregular basis, e.g., in 1996–2017, there were 16 sampling campaigns. When the lake was frozen in the winter period, sampling continued through a hole in the ice. From 2004, there was irregular sampling from the small pit lakes PL-2 and PL-3 (Figure 1B), which later formed in the quarry "Łom na Kapelance". In total, nine samples were taken from PL-2, and eight samples were taken from PL-3.

Electrical conductivity (EC), pH, and Eh were measured in situ using the WTW 330i unit, equipped with pH and SenTix ORP electrodes. From September 2010, the temperature of the surface layer in PL-1 was also measured together with sampling for Cl^- analysis.

In laboratory, alkalinity was determined by titration with HCl to an endpoint of 4.5, and concentration of Cl^- was determined using the argentometric method. In the Department of Hydrogeology of AGH in Krakow, Ca, Mg, Na, K, Fe, Sr, Zn, and Si were measured using ICP-AES Plasma 40. Major anions were analyzed by ion chromatography using the Dionex DX-120. Trace element concentrations were measured by ICP-MS (Perkin-Elmer, Elan 6100). The QA/QC was performed using certified materials. The concentration of nitrate was determined by colorimetry using a Hach Lange device. Reduced sulfur present as hydrogen sulfide was determined using the thiomercurimetric method.

The Eh–pH diagrams were prepared using the Geochemist's Workbench Professional 7.0 [30]. Table 1 presents a list of measured parameters and analyzed species.

Total contents of selected parameters of the bottom PL-1 sediments were determined using X-ray fluorescence (XRF).

Table 1. Measured parameters and analyses of samples, + analyzed, − not analyzed.

Parameter			**PL-1**	**PL-2**	**PL-3**
Air temp.		°C	+	−	−
Water level	-	m a.s.l.	+	−	−
Water temp.	Surface	°C	+	+	+
	Stratific.		+	−	−
pH	Stratific.	-	+	+	+
Eh		mV	+	+	+
EC		µs/cm	+	+	+
Ca^{2+}		mg/L	+	+	+
Na^{+}		mg/L	+	+	+
Mg^{2+}		mg/L	+	+	+
Cl^{-}		mg/L	+	+	+
$SO_4{}^{2-}$		mg/L	+	+	+
HCO^{3-}		mg/L	+	+	+
Fe		mg/L	+	+	+
Other parameters		mg/L	+	+	+

4. Results

4.1. Pit Lakes

Fluctuations of water level in pit lake PL-1 after the flooding period with a fast-rising water level were about 0.5 m in years with normal precipitation but reached 1.5 m in years 1997 and 2010 with extreme precipitation (Figure 4). Air temperature measured in the period from September 2010 to December 2018 was in the range from −23 °C to 36 °C. The temperature of the surface water layer measured close to the NW bank of the pit lake followed the changes in air temperature (Figure 5). Temperatures in winter ranged from 0.2 °C to 4.1 °C. In the temperature plot, three consecutive warm winters can be identified where the surface temperature increased from 2.5 °C in 2014 to 4.1 °C in 2016.

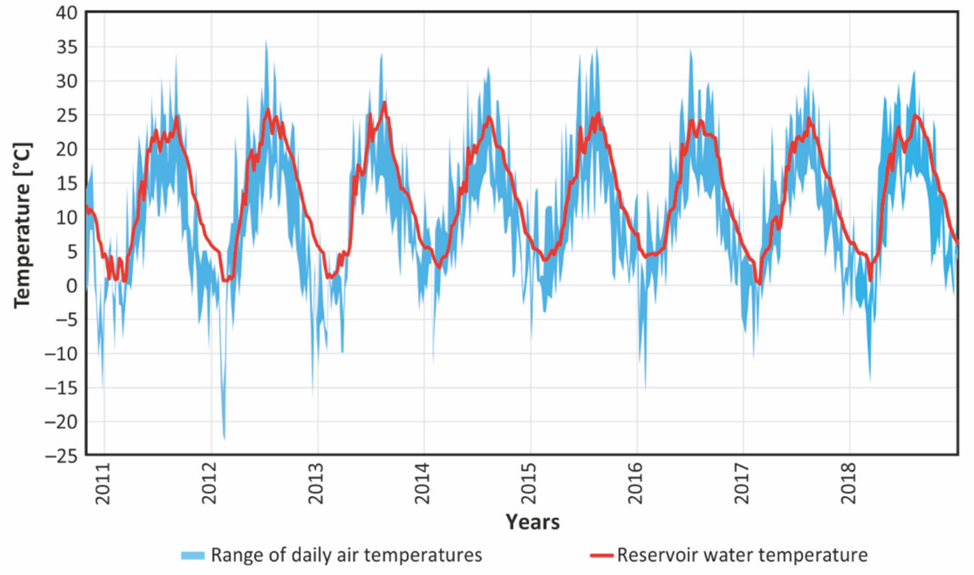


Figure 5. Air and water surface layer temperature fluctuations in period 2010–2018.

In the period from May 2003 to October 2013 there were six measurements of water temperature on vertical profiles in the pit lake PL-1. Measurements were taken in the deepest part of the pit lake and close to its western limit. From May to September, all profiles were similar (Figure 6). Three zones typical for deep lakes were identified [26]: epilimnion, metalimnion (thermocline sensu Golterman [31]), and hypolimnion. The epilimnion with temperatures of 20–21 °C extended to a depth of 9–10 m, the metalimnion was at a depth of about 20 m where temperature decreased to 7–10 °C, and the hypolimnion extended down to the bottom with temperature of 5–6 °C. In October 2013, only the epilimnion with a temperature of 14 °C to the depth of 10 m and metalimnion with a temperature of about 5 °C at a depth of 28 m were found (see Figure 6).

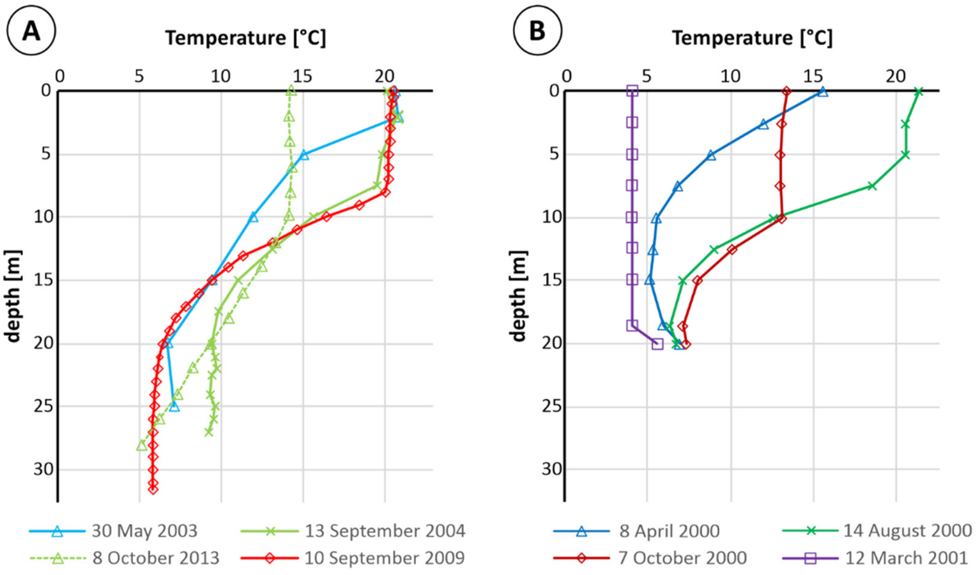


Figure 6. Temperature of water in PL-1: (**A**) measured values; (**B**) data after [32].

Galas [32] measured temperatures down to a depth of 20 m from April 2000 to March 2001. Homothermic conditions occurred from April to December, epilimnion and metalimnion occurred in May, and all three zones including hypolimnion were identified in the remainder of the year.

Values of electric conductivity (EC) in PL-1 are shown in Figure 7. Initially, after flooding, there was a distinct EC stratification reaching almost 1600 µS/cm in May 2003 at 25 m depth, but only 1200 µS/cm in the surface layer. The stratification continued in subsequent years, but EC values on the profile decreased gradually. Finally, the stratification disappeared in September 2009, when the EC values were relatively constant with depth and close to 1100 µS/cm, further decreasing to less than 1000 µS/cm in August 2013.

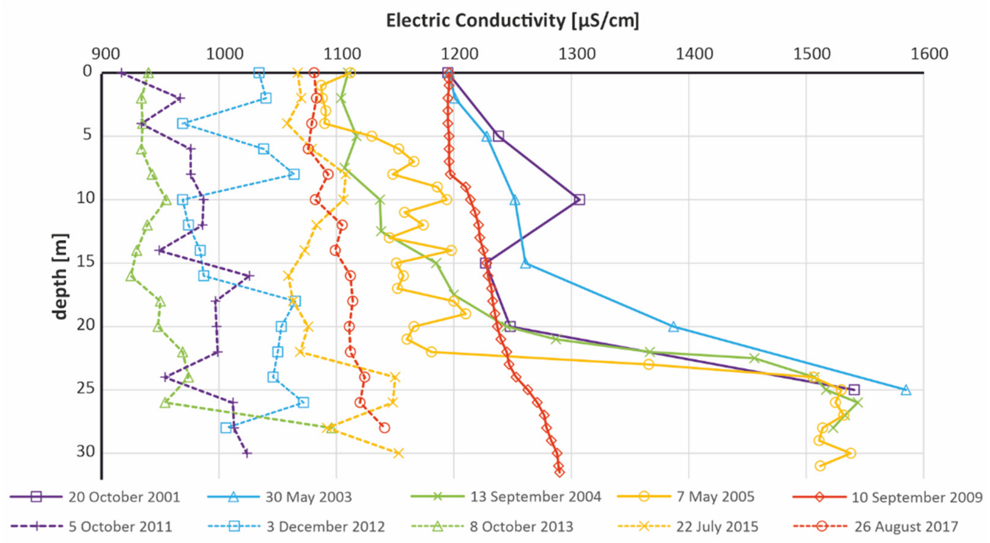


Figure 7. Values of electrical conductivity in PL-1.

The concentration of Cl^- in water pumped from "Zakrzówek" quarry from December 1991 to November 1992 ranged from 106 to 348 mg/L, with an average of 240 mg/L [29]. During flooding, 3 samples were taken in February and March 1996, and Cl^- concentrations ranged from 272 to 286 mg/L.

During the period from February 1998 to December 2018, the concentration of Cl^- in the surface water layer decreased from 210 mg/L to 130–140 mg/L, i.e., with an average decreasing concentration rate of about 3.5 mg/L per year, but the dynamics of the process was variable (Figure 8).

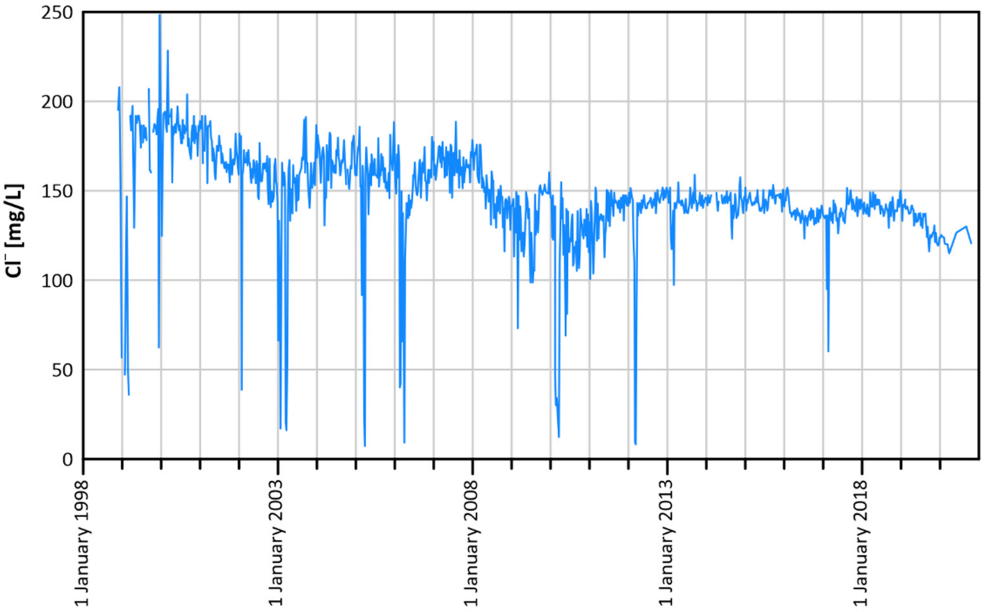


Figure 8. Concentration of chloride in surface layer of PL-1.

Values of pH in the vertical profile of PL-1 ranged from 6.8 to 8.7 without significant temporal changes and with a slightly decreasing trend with depth (Figure 9).

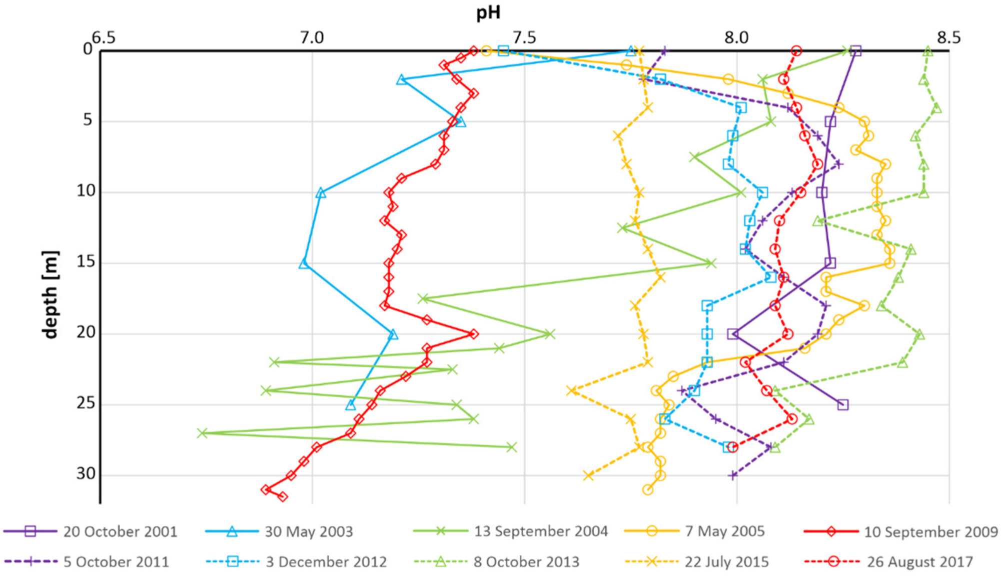


Figure 9. Values of pH vs. depth in pit lake PL-1.

In 2003 values of Eh measured at the depths between 0 and 5 m were from 292 to 302 mV and decreased to −158 mV at the depth of 25 m. In 2004, Eh values were between 422 and 454 mV down to 20 m depth, decreased to 129 mV at 20 m depth and to −87 mV at 25 m depth, and then slightly increased to −58 mV at the bottom at 28 m depth (Figure 10).

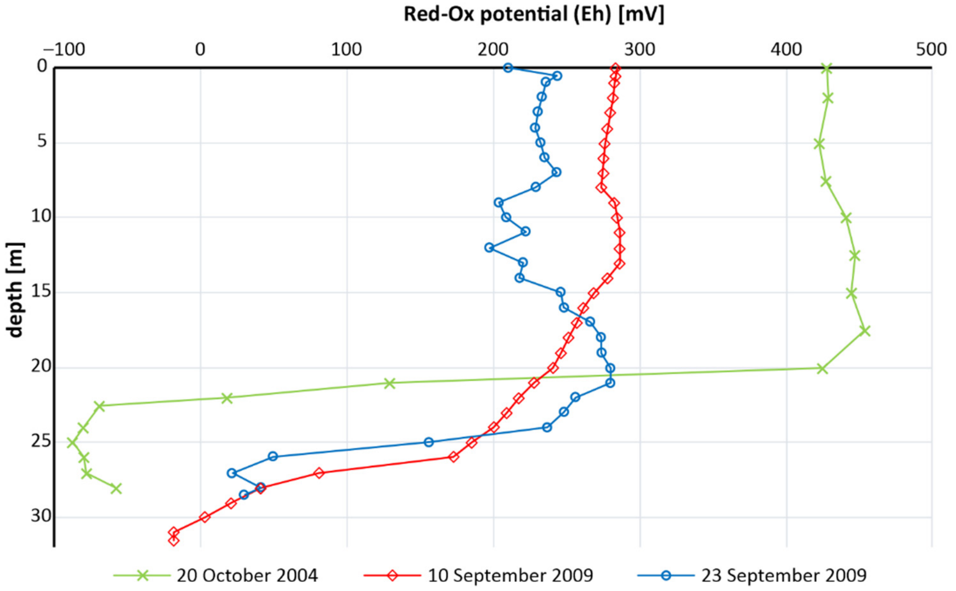


Figure 10. Values of Eh value vs. depth in pit lake PL-1.

In September 2009, the Eh values were measured on two profiles: at the site where depth reached 31.5 m (Profile I) and at the western wall of the quarry (Profile II). In Profile I, the Eh values ranged from 274 mV to 286 mV down to 14 m depth and then decreased to 173 mV at 26 m. From this depth, there was fast drop to 80.5 mV at 27 m and then to −19 mV at 30 and 31.5 m depths (Figure 10). In Profile II, the trend was different; there was almost no change down to 24 m depth with an Eh value of 197 mV at 12 m depth, which increased to 280 mV at 20–21 m depth. Below 25 m, Eh values ranged from 22 to 50 mV (Figure 10).

Changes in Cl^- stratification are an important indicator of water chemistry evolution in PL-1 from the viewpoint of the inflow of contaminated Vistula River water during the pit flooding. The process lasted from November 1992 to July 1997. In that period, the concentration of Cl^- in Vistula River ranged from 42.8 to 2005 mg/L, with an average of 1029 mg/L [29].

There was a significant evolution over time. First profiling performed in winter 1996 showed that Cl^- concentration gradually increased with depth (Figure 11). In later profiling measurements (2001–2005), a distinct chemocline at s depth of about 20 m was confirmed. Below this depth, the concentration increased by several tens of mg/L. In the next few years, Cl^- concentration decreased; in the 2015–2017 period, the concentration in the surface layer was 143 mg/L, while it was 158 mg/L below 20 m depth (Figure 11).

The concentration of sulfate in the vertical profile of PL-1 until 2005 showed, down to 22–24 m, a moderately increasing trend before decreasing in deeper zones. In the next few years, the concentration decreased in general, but there was a mild trend of increase with depth (Figure 12). In 1996, the concentration of sulfate ranged from 238 to 263 mg/L; in 2017, it ranged from 156 to 164 mg/L (Table 2). The concentration of bicarbonate in PL-1 in most profile data showed an increase with depth.

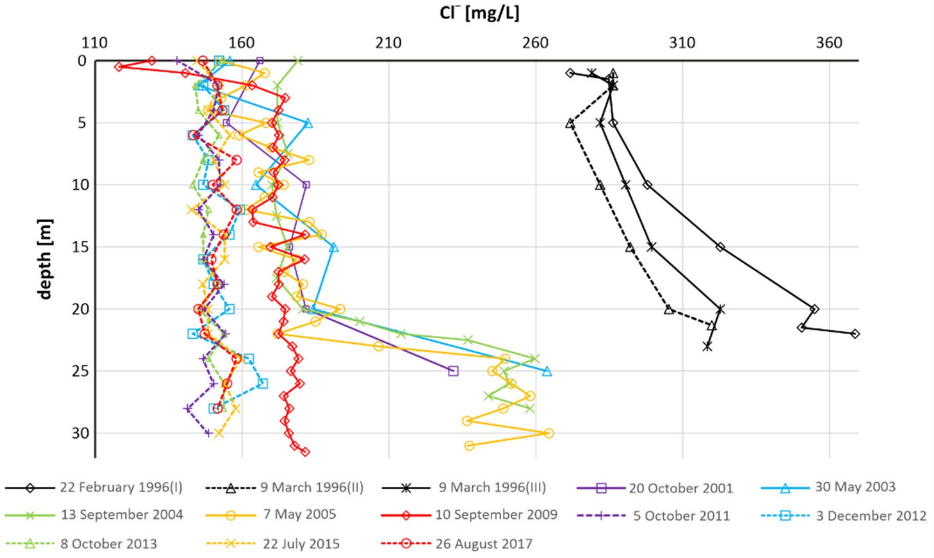


Figure 11. Concentration of chloride vs. depth in pit lake PL-1.

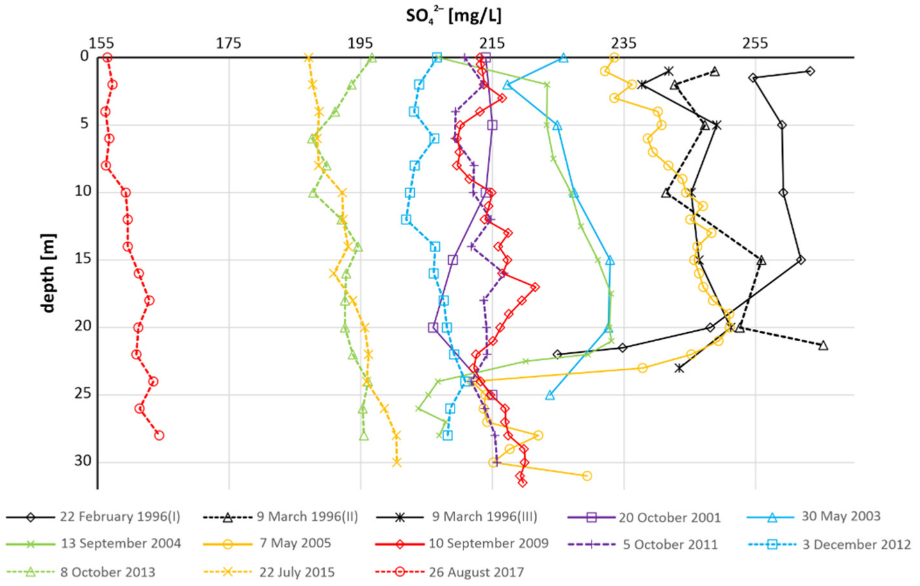


Figure 12. Concentration of SO_4^{2-} vs. depth in pit lake PL-1.

Table 2. Extreme values of EC, pH, and concentrations of major ions in PL-1 profiles; n.m.—not measured.

Parameter			1996	2001	2003	2004	2005	2009	2011	2012	2013	2015	2017
EC	µS/cm	min.	n.m.	1195	1196	1104	1087	1195	917	969	925	1058	1076
		max.	n.m.	1541	1585	1544	1538	1290	1026	1072	1096	1153	1141
pH	-	min.	n.m.	8.0	7.0	6.7	7.4	6.9	7.8	7.5	8.1	7.6	8.0
		max.	n.m.	8.3	8.3	8.3	8.4	7.4	8.2	8.1	8.5	7.8	8.2
Ca^{2+}	mg/L	min.	130	74	106	105	110	104	106	85	97	98	85
		max.	158	94	151	141	144	117	116	116	102	106	95
Mg^{2+}	mg/L	min.	41	31	27	35	35	33	32	33	31	31	31
		max.	49	42	39	46	46	37	35	34	32	32	32
Na^{+}	mg/L	min.	149	95	81	94	92	95	89	86	81	75	83
		max.	192	154	129	139	133	105	95	100	87	77	86

Table 2. *Cont.*

Parameter			1996	2001	2003	2004	2005	2009	2011	2012	2013	2015	2017
K^+	mg/L	min.	7.9	10.2	11.2	9.4	9.4	9.3	9.2	9.1	8.3	7.6	7.7
		max.	9.4	11.1	13.5	12.5	11.4	10.1	9.4	9.7	8.8	7.8	8.0
HCO_3^-	mg/L	min.	222	164	156	143	155	201	197	157	166	153	201
		max.	335	257	308	330	291	268	254	285	255	228	231
SO_4^{2-}	mg/L	min.	226	206	217	207	215	205	209	202	192	187	156
		max.	263	215	233	233	251	221	217	215	199	200	164
Cl^-	mg/L	min.	272	155	145	170	153	118	138	143	141	143	143
		max.	368	232	264	258	237	181	154	167	164	158	158

Changes in the major cation concentrations in the profiles presented various patterns, but regular trends were observed. The first general trend was an increase in concentration with depth, and the second trend was a decrease in concentration over time. The fastest-decreasing trend was observed for Na^+ and Ca^{2+}, whereas it was moderate for Mg^{2+} and the least for K^+ (Table 2).

The concentration of Na^+ correlated well with the concentration of Cl^-, $R^2 = 0.876$ (Figure 13), in good agreement with by far the most important origin of these ions in Vistula River contaminated by NaCl brines pumped from mines.

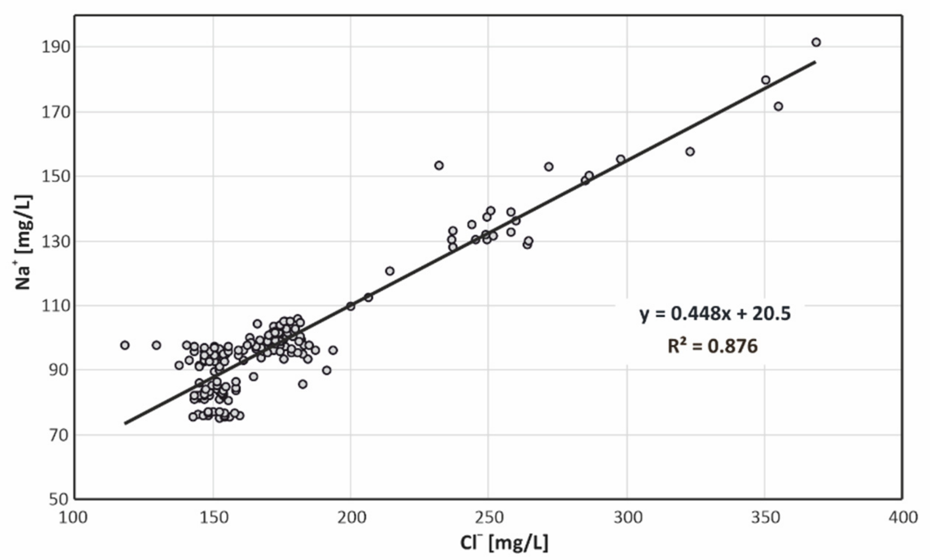


Figure 13. Correlation of Na with Cl in PL-1.

Concentrations of Ca^{2+} (Figure 14) and Mg^{2+} (Figure 15) showed decreasing trends over time, but they increased below 20 m depth until 2004. In the later period, concentrations of both ions became uniform with depth and gradually decreased over time. Concentrations of Mg in 2003 were lower than those in 2001 and 2004 (Table 2). The concentration of K showed an increasing trend until 2003 and then a decreasing trend in the subsequent years (Table 2).

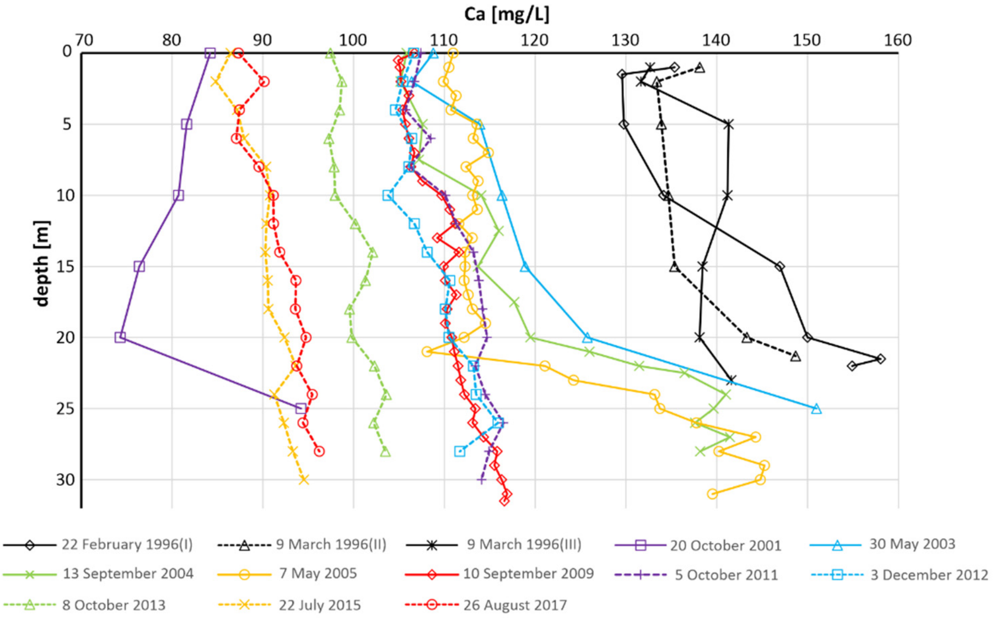


Figure 14. Concentration of Ca vs. depth in PL-1.

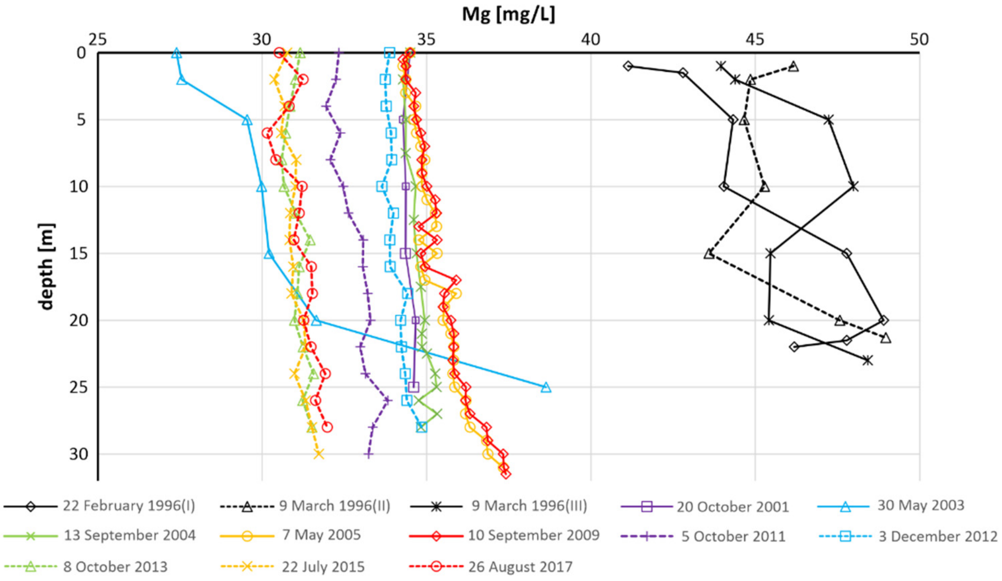


Figure 15. Concentration of Mg vs. depth in PL-1.

In general, there was a trend of decreasing concentrations for all trace elements over time except for boron (Table 3). The concentration of Ba in PL-1 varied between 0.028 and 0.11 mg/L, while the concentration of Li ranged from 0.01 to 0.046 mg/L, except for the years 2004 and 2005, when they were lower.

In 1996, when the water table was still 5 m below its maximum level, the concentration of iron in Profile I down to 10 m depth was less than 0.001 mg/L, but increased to 0.037 mg/L at 15 m and then to 0.26 mg/L at depth 22 m. In Profile II, iron was below detection limit down to 15 m, at 20 m reached 0.052 mg/L and then 0.13 mg/L at 21.3 m (Figure 16). In Profile III iron was below detection limit down to 23 m.

Table 3. Extreme concentrations of trace elements in PL-1 profiles (n.m.—not measured).

Microelement (µg/L)		1996	2001	2003	2004	2005	2009	2011	2012	2013	2015	2017
Fe	min.	<10	n.m.	9.0	1.0	2.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
	max.	962	n.m.	48	132	28	4	11	1	4	<1.0	15
Mn	min.	<2.0	0.4	1.6	0.2	0.5	0.1	0.2	<1.0	<0.5	<0.5	<0.5
	max.	372	1.1	278	245	172	0.9	9.4	4.0	2.4	<1.0	1.2
Ba	min.	59	50	54	64	48	57	51	63	50	28	44
	max.	98	55	74	109	102	78	58	90	61	37	46
Sr	min.	1610	890	810	1260	104	1150	1020	1100	1020	105	92
	max.	2010	1120	1290	1940	1810	1430	1160	1290	1120	114	109
Ni	min.	n.m.	2.6	<0.1	1.2	1.1	1.0	2.1	<0.1	7.9	3.6	1.7
	max.	n.m.	4.3	<0.1	4.7	3.3	3.2	3.2	0.7	13	4.5	2.3
Br	min.	n.m.	400	1210	510	450	270	330	310	40	250	510
	max.	n.m.	580	1780	830	720	700	370	510	58	280	530
I	min.	n.m.	15.1	<1.0	11	9.4	4.8	<1.0	3.1	<1.0	11.7	<1.0
	max.	n.m.	24.9	29.1	37.0	27.2	9.2	<1.0	31.9	10.8	36.4	<1.0
B	min.	630	530	450	600	700	720	530	270	350	430	810
	max.	830	630	640	870	1000	810	620	580	610	500	850
PO4	min.	n.m.	5	620	30	25	16	8	<1.0	50	180	29
	max.	n.m.	17	890	130	140	140	16	99	150	260	46

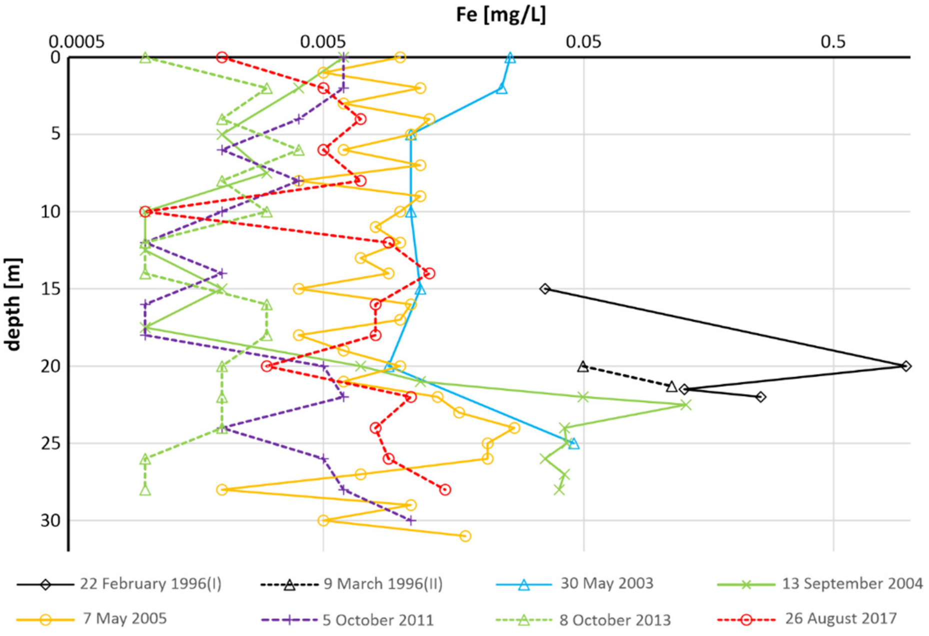


Figure 16. Concentration of iron vs. depth in PL-1.

In Profile I, manganese was below the detection limit down to 5 m depth, before increasing to 0.017 mg/L at 10 m, 0.37 mg/L at 20 m, and 0.31 mg/L at 21.5 m. In profile II, the manganese concentration was below the detection limit down to 15 m and increased to 0.14 mg/L at 20 m. In Profile III, manganese was below the detection limit down to 10 m, and then increased to 0.007 mg/L at 15 m, 0.14 mg/L at 20 m, and 0.2 mg/L at 23 m (Figure 17).

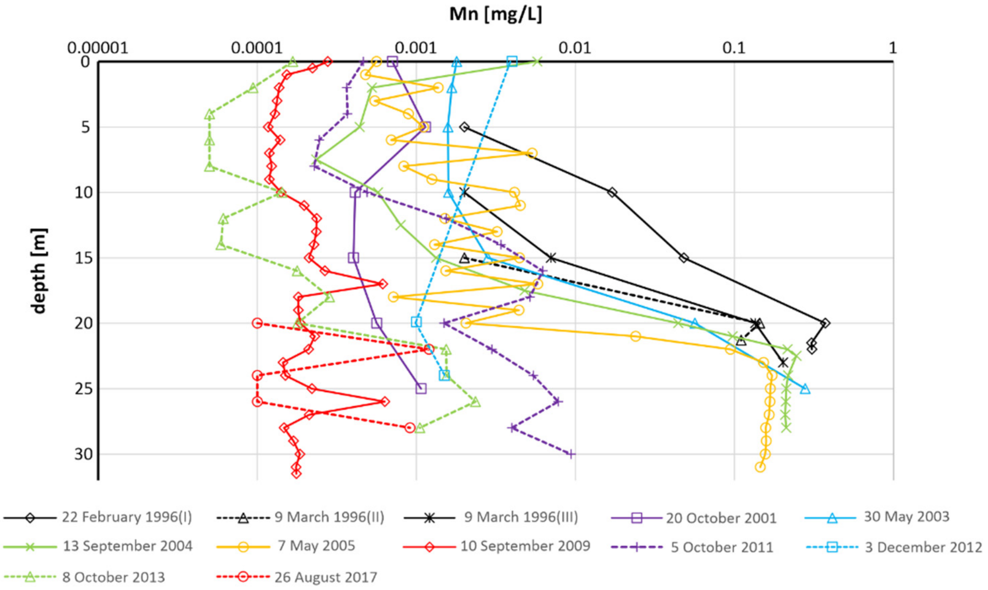


Figure 17. Concentration of manganese vs. depth in PL-1 (a lack of data indicates concentrations below the detection limit of 0.002 mg/L in 1996 and below 0.00005 mg/L from 2001 onward).

In 2001 and 2003, concentrations of both iron and manganese on profiles in PL-1 increased with depth. This was consistent with Eh trends (Figure 10) and the more reducing conditions at greater depth, whereby Eh changed from 454 mV at 20 m to 129 mV at 21 m and then decreased to −87 mV at 25 m before slightly increasing to −58 mV at 28 m.

After homogenization of the water chemistry with depth from about 2009, iron concentrations were about 0.001 mg/L and manganese concentrations were between 0.0001 mg/L and 0.00093 mg/L. In the same period, the concentration of manganese decreased significantly. In 2013, manganese was below the detection limit of 0.00005 mg/L down to 16 m depth and increased to 0.022 mg/L at 28 m depth.

In 2005, the concentration of iron in the PL-1 profile was rather stable with a maximum at 24 m depth. Manganese showed a similar behavior to earlier (Figure 17).

The concentration of strontium in early years showed strong stratification and decreased over time (Figure 18). In 1996, the concentration of Sr was at maximum, and stratification was limited. From 2005, the concentration increased below 22–25 m; however, in the subsequent years, the differences in profiles decreased, and concentrations ranged from 0.092 to 0.114 mg/L.

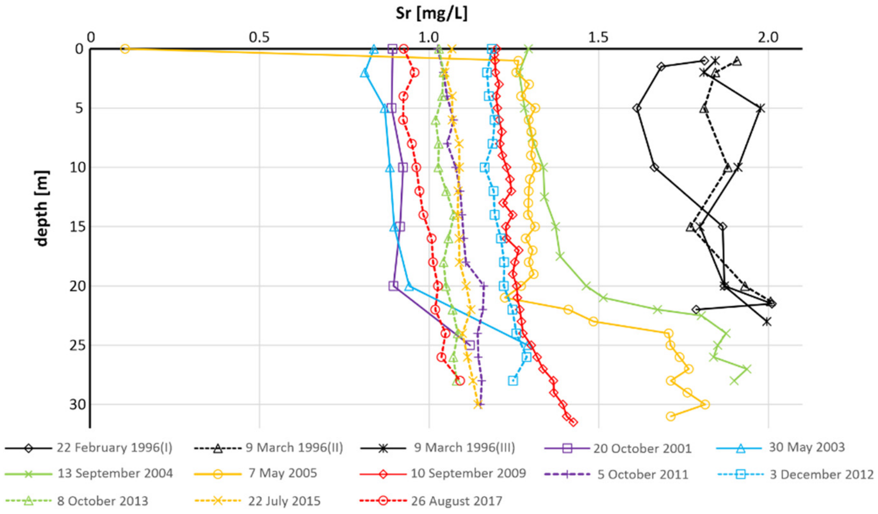


Figure 18. Concentration of strontium vs. depth in PL-1.

Initially, concentrations of Br showed stratification; in 2009, they ranged from 0.27 to 1.78 mg/L and increased with depth. In subsequent years, the concentrations were lower, and the stratification disappeared. The behavior of I was similar, and concentrations ranged from below the detection limit to 0.042 mg/L.

The concentration of B increased with depth until 2004 and then was almost stable. In 2004, there was sampling for hydrogen sulfide, H_2S. It was undetectable down to the depth of 20 m; however, its concentration reached 0.34 mg/L at 21 m and even 61.6 mg/L at 24 m. In the depth interval of 25–28 m, the concentration slightly decreased to 53.6–58.3 mg/L, in good agreement with the Eh trend (see Figure 10).

Pit lakes PL-2 and PL-3 were formed in the late stage of flooding of the quarry "Łom na Kapelance" close to its eastern wall (Figure 1B). They are ephemeral lakes about 0.5 m deep, drying occasionally. During intense precipitation in 2010, both lakes merged, and PL-4 was formed with a depth of 2 m.

In PL-2, water was less mineralized compared to PL-3. The value of TDS ranged from 385 to 685 mg/L (Table 4), and water was of the $Ca–HCO_3$ or $Ca–HCO_3–SO_4$ type. Concentrations of Ca^{2+} ranged from 60 to 182 mg/L, concentrations of Mg ranged from 4.8 to 10 mg/L, concentrations of Na ranged from 6.2 to 18 mg/L, and concentrations of K ranged from 4.9 to 15 mg/L. The concentration of HCO_3^- was as high as 412 mg/L, that of SO_4^{2-} was as high as 249 mg/L, and that of Cl^- was as high as 34 mg/L. In PL-3, water was less mineralized, with TDS ranging from 321 mg/L to 435 mg/L; water was of the $Ca–HCO_3$ type. Concentrations of major ions were slightly lower than in PL-2 (Table 4).

Table 4. Extreme values of EC, pH, and concentrations of major ions in PL-2, PL-3, and PL-4.

Pit Lake	Value	pH	EC	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	SO_4^{2-}	Cl^-	NO_3^-	TDS
		-	µS/cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
PL-2	min.	7	485	62	4.8	5.2	4.9	198	14.3	14.2	9.2	386
	max.	7.8	757	182	10.1	17.8	14.9	412	249.1	33.7	21.6	685
PL-3	min.	7.1	360	53	4.1	1.0	2.9	155	8.4	7.3	7.9	321
	max.	7.8	501	101	8.4	7.2	49.4	309	8.4	13.2	10.0	470
PL-4	-	7.7	451	95	7.8	7.3	5.8	272	49.1	15.6	n.m.	452

Water chemistry parameters of the new lake were between those of PL-2 and PL-3 with a TDS of 452 mg/L, and water was of the $Ca–HCO_3$ type.

Concentrations of trace elements in PL-4 were generally between maximum concentrations in PL-2 and PL-3 and closer to their minimum values (Table 5).

Table 5. Extreme values of selected trace elements in PL-2, PL-3, and PL-4.

Pit Lake	Value	Fe	Mn	Ba	Sr	Ni	Br	B	PO_4^{3-}	Zn	Li	Al	As
		µg/L											
PL-2	min.	<1.0	1.1	21	181	0.9	<1.0	43	35	<1.0	1.9	1.3	1
	max.	197	237	367	413	3.1	41	182	1880	81	9.6	7.8	3.1
PL-3	min.	<1.0	0.1	28	94	0.7	<1.0	4.8	52	<1.0	1.3	1.2	<0.1
	max.	102	4.4	448	377	1.7	219	88	231	51	10.5	5.9	2.4
PL-4		31	9.1	161	229	1.1	15	171	107	7.8	2.6	22.5	3.4

4.2. General Water Chemistry Trends and Water Types

In the period of "Zakrzówek" quarry flooding, the inflow of Vistula River NaCl contaminated water with a mineralization of more than 400 mg/L was the principal factor responsible for the PL-1 water chemistry. In the rare high stages of Vistula River, water in the river was of the $Na–Ca–HCO_3–Cl–SO_4$ type, $Ca–Na–Cl–HCO_3$ type, or $Na–Ca–Cl–HCO_3$ type (Figure 19). During the flooding, water from Vistula River was mostly of the Na–Cl type, but concentrations of Mg^{2+} were 40–70 mg/L, while those of $SO_4{}^{2-}$ were 100–200 mg/L, i.e., an order of magnitude higher than concentrations reported for groundwater from the Upper Jurassic in Krakow–Częstochowa Upland [33–35].

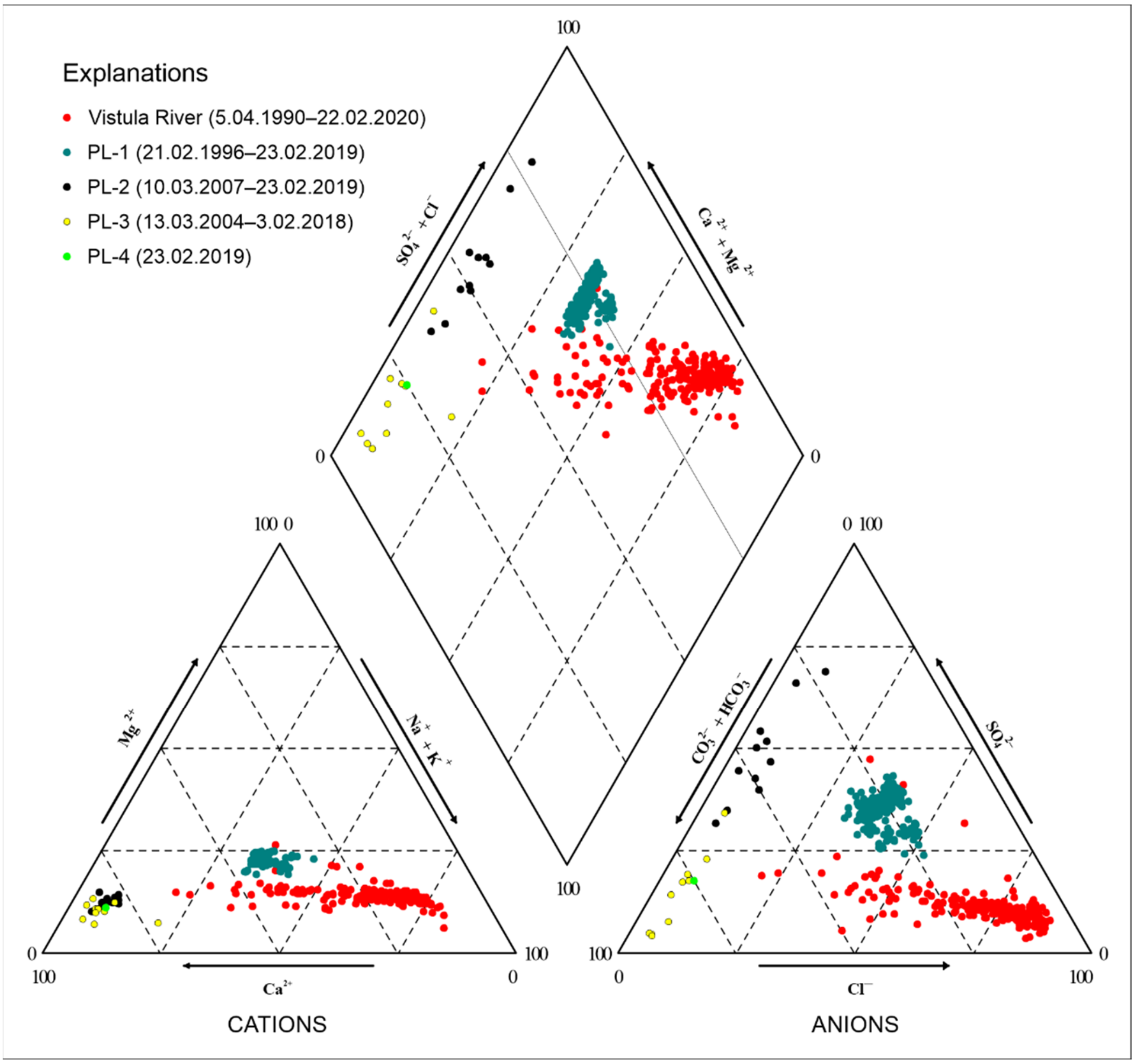


Figure 19. Piper diagram for water samples from pit lakes and Vistula River.

Later, the mixing of Vistula River water and precipitation water resulted in several other ions present in PL-1. In the period from 1996 to 2018, Na^+ was the dominant ion; only in 1996 was Ca^{2+} dominant at the bottom of the pit lake. Anions Cl^- and $SO_4{}^{2-}$ generally dominated until 2015, whereas, from 2017, the order changed to Cl^- followed by $HCO_3{}^-$. In smaller pit lakes (PL-2, PL-3, and temporary lake PL-4), the water chemistry was dominated by wall chemistry and was clearly separated from Vistula River and PL-1 in the Piper diagram (Figure 19). Ca^{2+} and $HCO_3{}^-$ were always dominant, but $SO_4{}^{2-}$ was also significant, especially in PL-2.

4.3. Composition of PL-1 Lake Bottom Sediments

The composition of the PL-1 lake sediments sampled and analyzed in 2005 is presented in Table 6. In sediments of PL-1 sampled and analyzed in 2005, total iron content was as high as 11 g/kg, Ca content was as high as 263 g/kg, and Si content expressed as SiO_2 was as high as 186 g/kg.

Table 6. Composition of sediments at the bottom of PL-1.

	Ca	**SiO_2**	**Fe**	**S**	**Al**	**Mg**	**Zn**	**K**	**P**
Parameter (mg/kg)	263,300	186,400	10,950	7100	6360	4190	2900	2360	392
	Mn	**Na**	**Ba**	**B**	**Pb**	**Ni**	**Cr**	**V**	**Rb**
	170	143	132	23.9	9.05	7.55	4.72	4.04	3.55
	Li	**As**	**Zr**	**Y**	**Co**	**Ga**	**U**	**Cd**	**Mo**
	2.34	1.89	1.75	1.74	1.69	1.26	0.26	0.26	0.22

5. Discussion

The water chemistry in the pit lakes in Zakrzówek is determined by internal and external factors. The principal internal factor is the composition of rocks where the chemistry of the groundwater recharging lake was formed. Depending on the solubility of rock minerals, the water in pit lakes can range from fresh in metamorphic rocks [36] to highly mineralized in pit lakes located in sedimentary rocks rich in minerals such as gypsum [33]. External factors are sources of contamination around pit lakes.

The main reason for the changes in water chemistry and the transition from a meromictic to holomictic regime over time in PL-1 was the dilution by groundwater formed by recharge flowing to the pit lake and direct precipitation onto the pit lake surface. After complete filling of PL-1, the flow direction changed from Vistula River to the pit lake, instead flowing from the pit lake to Vistula River (Figure 2B). Another factor contributing to the changes in water chemistry is the thermal circulation in the pit lake. In fall/winter, the period temperature of the surface water is below 4 °C, and surface water mixes with deeper water. The initially highly mineralized dense water limited the exchange with shallow layer, and conditions were meromictic. However, the process was not unidirectional, as indicated by Cl^- concentration changes in the surface layer and vertical profile (Figures 8 and 11). Until 2005, water exchange reached the depth of 20–22 m, and the Cl^- concentration profile became uniform. This was in good agreement with the profiles of EC (Figure 7); when initial stratification disappeared in about 2009, profiles became almost equal in later years, and holomictic conditions prevailed.

The changes in the Cl^- concentration in the profile were linked to its changes in the surface layer with general trends of decreasing concentrations and decreasing fluctuation (Figure 11). In the first period of monitoring (1998–2003), when atmospheric precipitation followed the long-term trend, the concentration decreased, but the amplitude of fluctuations was high. Years 2003–2007 were dry with a resulting low water level in PL-1 and temporarily reversed direction of flow from Vistula River to PL-1. More mineralized water started to return to the pit lake, and the Cl^- concentration in the surface layer increased again. In subsequent years, when the water level in PL-1 increased again, the Cl^- concentration decreased, before stabilizing from 2011 at about 150 mg/L and even decreasing to 140 mg/L in 2016. The observed stabilization of Cl^- concentration in the surface layer was consistent with its stabilization in the complete water column (Figure 11).

Two major processes caused changes in the sulfate concentration in PL-1: dilution and initially strongly reducing conditions. Before PL-1 flooding, ther grass, small trees, bushes, and fauna such as snails and other small animals could be found at the bottom of the quarry. After flooding, all organic matter fell below the water table, and its decomposition resulted in reducing conditions with a resulting reduction of sulfate. This process occurs when electron donors such as reactive organic matter and sulfate-reducing bacteria (SRB) are present [37,38], whereby sulfate is reduced, followed by the formation of H_2S and potential precipitation of secondary sulfide minerals. During the sampling campaign in 1996, hydrogen sulfide was detected in two profiles from 15 m depth and in one profile from 20 m depth. The reduction zone with H_2S decreased in size over time: from 21 m in 2004 to 26–27 m in 2009, before completely disappearing in 2011 in all profiles, probably due to the decrease in reactive organic matter content.

During water turnover, when the temperature of water was equal in all profiles, reduced and oxidized waters mixed. Until 2005, sulfates in the deep zone underwent a reduction process and the concentration decreased (Figure 12). This was demonstrated in the analyses of water from March 1996, when the concentration of sulfate decreased below 15 m depth.

In the Eh–pH diagram for samples monitored in 2004 and 2009, all points were in the field of sulfate, but they approached the H_2S field in the deep zone (Figure 20). After 2011, when H_2S was no longer detected, the concentration of sulfate was affected by precipitation dilution and input from Vistula River.

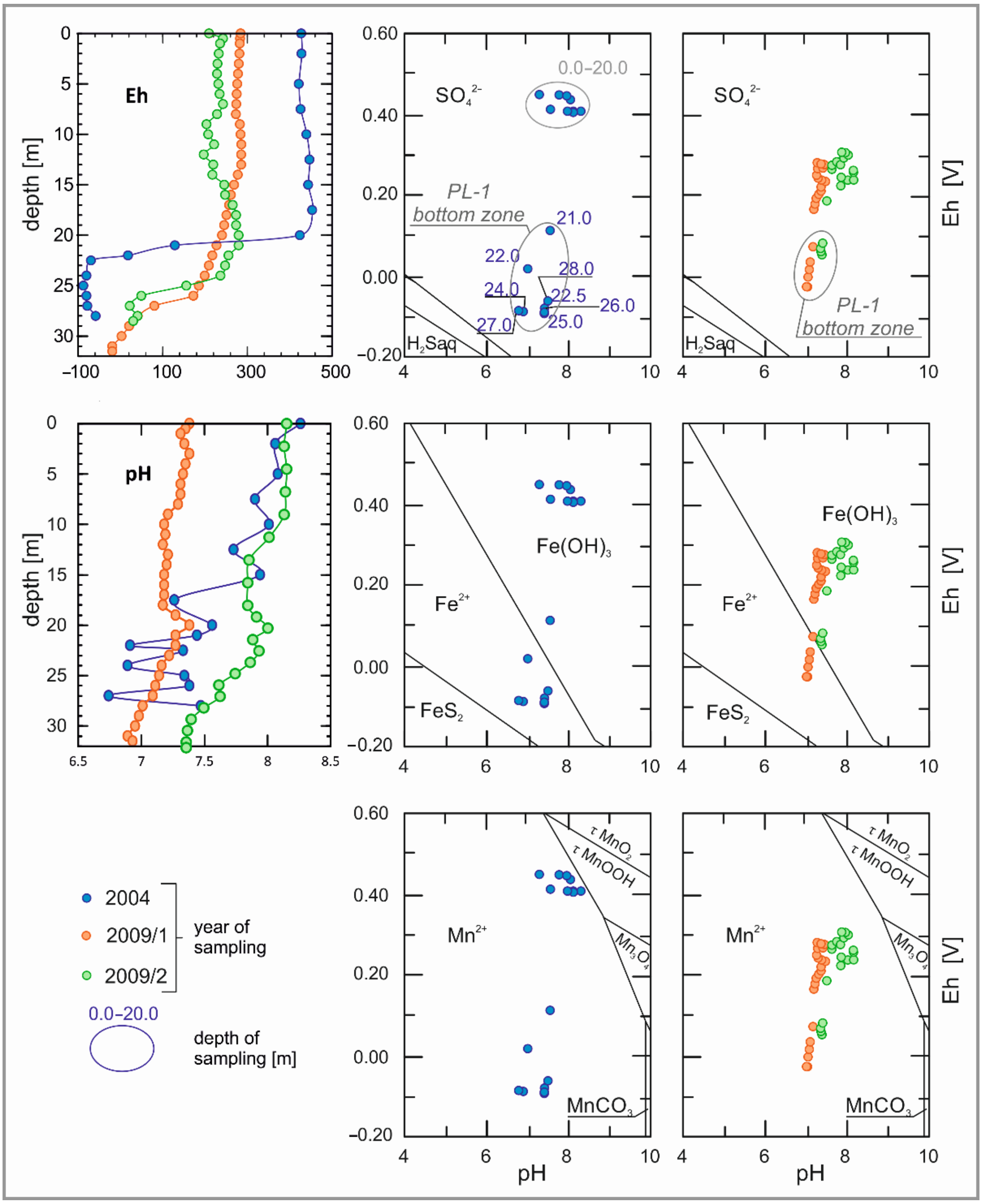


Figure 20. Diagrams for PL-1: plots of Eh and pH vs. depth and Eh–pH diagrams for S, Fe, and Mn based on their average concentrations.

Concentrations of major cations were also affected by atmospheric dilution and the input from Vistula River, depending on the change in flow direction. Changes in Na^+ followed Cl^- changes, whereas Mg^{2+} generally decreased over time, and Ca^{2+} depended on $HCO_3{}^-$ concentration. As a result, in the deep reducing zone, where CO_2 was produced by the decomposition of organic matter [39], concentrations of Ca^{2+} and Mg^{2+} were higher than in the shallow zone (Figures 14 and 15).

Concentrations of Fe and Mn depended on redox conditions. Until 2004, values of Eh ranged from 400 to 500 mV down to the depth of 20–21 m and then decreased in the deeper part of the profile [40]. In 2003, Eh at the bottom was −158 mV, whereas it reached −87 mV below 18 m in 2004 (Figure 11). In the deep zone with reducing conditions, concentrations of Fe and Mn increased, and they were present mostly as free ions (Fe^{2+} and Mn^{2+}) (Figure 20).

Iron is soluble, as Fe^{2+} and its concentrations were very high in the reducing zone (Figure 16); the same applies to manganese soluble as Mn^{2+} (Figure 17). During sampling of PL-1, a dark suspension settling down was observed below 20 m, probably mostly composed of precipitated reduced iron phases. The content of total iron in PL-1 sediments was considerable (Table 6). This is in a good agreement with the presence of authigenic sulfide minerals confirmed in lakes with reducing conditions in their hypolimnion (e.g., [41]). Precipitated iron sulfide phases may contain other trace elements.

Small pit lakes PL-2 and PL-3 were in hydraulic contact with PL-1, and they represented water flowing to PL-1 from the east. They had a $Ca–HCO_3$ water type (Figure 19), modified by external factors. Initially, from 2004 to 2009, concentrations of sulfate were high, and water was of the $Ca–HCO_3–SO_4$ type. Sulfate was probably of geogenic origin because of the close contact with Miocene clays rich in gypsum.

Trees surround pit lake PL-2; thus, leaves and organic litter fall into the water. Pit lake PL-3 is surrounded by grassy areas, and there is less input of organic matter. Around both lakes, there are rocks attended by climbers and tourists, contributing to anthropogenic contamination, with elevated concentrations of nitrate and phosphate, especially in PL-2 (Tables 4 and 5).

The presented results are consistent with other comprehensive studies of contamination by anthropogenic activities and saltwater intrusions (e.g., [42–45]).

6. Conclusions

In the Zakrzówek horst area, there was exploitation of Upper Jurassic limestones in two quarries. The older one (Łom na Kapelance) was exploited to the groundwater table level, while the younger one (Zakrzówek) was exploited to the level 36 m below the groundwater table. Vistula River contaminated by NaCl brines from the Upper Silesia Basin about 80 km west of Krakow flows 700–900 m from the Zakrzówek horst, and it was the main source of water inflow to the quarries from 1992 to 1997, when the water level in “Zakrzówek” quarry reached an elevation about 0.5 m above the average water level in Vistula River. When flooding ceased, Vistula River became a drainage base, and the groundwater flow direction reversed.

At the time of flooding, there was a mixing of Vistula River water and precipitation water, thus recharging the limestone aquifer at the Zakrzówek horst. In the period from 1996 to 2018, the dominant cation in the pit lake PL-1 was Na. Until 2015, anions Cl^- and $SO_4{}^{2-}$ were dominant, while $HCO_3{}^-$ was also significant.

The changes in the water chemistry in PL-1 after flooding were caused by both external and internal factors. The principal external factor was the reversal of flow toward Vistula River with resulting freshening of water in PL-1. In temporary dry periods, the water level in the pit lake was lower in comparison to that in Vistula River. Hence, flow direction reversed again, followed by a temporary increase in mineralization in PL-1.

The meromictic stratification in principal lake observed in PL-1 after flooding, with high concentrations of Cl and other ions close to the pit lake bottom, was a consequence of the contaminated water inflow from Vistula River during flooding. After the flooding, there was freshening of the surface layer due to recharge from precipitation and the mixing of fresher surface water with deep mineralized water due to thermal circulation caused by spring and fall turnovers and holomictic conditions. The second factor was redox zonation with the oxidized layer at the top and the reduced layer at the bottom. In the deep layer, sulfate was reduced, hydrogen sulfide was formed, and Fe and Mn concentrations increased. The reducing zone decreased in size over time, and, about 20 years after flooding, the oxidized zone completely occupied the water column in the pit lake because of holomictic conditions.

The results of the study clearly demonstrate the importance of the connection between surface water bodies and water in mining pit lakes. Initially, the water chemistry was dependent on the external water input and meromictic conditions, with a clear stratification and redox zonation present. These conditions were only temporary, and the freshening of surface water due to recharge from precipitation and thermal circulation resulted in homogenization of the mineralization and more oxidizing, holomictic conditions in the complete water column. Nevertheless, fluctuations of the water level in the PL-1 pit lake and new input of water from Vistula River could reverse the observed trends; thus, the water chemistry should be monitored in the future. A limitation of this study is the long intervals between measurements and sampling. In the future, key parameters can be monitored by data loggers. In summary, the transition from meromictic to holomictic conditions in mining pit lakes is possible under specific conditions.

Author Contributions: Conceptualization, J.M., K.d. and A.P.; methodology, J.M. and O.S.; validation, J.M., K.d. and A.P.; formal analysis, O.S.; investigation, J.M. and M.Ź.; data curation, K.d. and M.Ź.; writing—original draft preparation, J.M.; writing—review and editing, A.P. and O.S.; visualization, K.d., M.Ź. and A.P.; supervision, J.M., O.S. and A.P.; funding acquisition, A.P. and K.d. All authors read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: This study was partially supported by the Polish Ministry of Education and Science, as part of the subsidy to the AGH University of Science and Technology in Krakow, Faculty of Geology, Geophysics, and Environmental Protection (16.16.140.315).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Gammons, C.H.; Harris, L.N.; Castro, J.M.; Cott, P.A.; Hanna, B.W. Creating lakes from open pit mines: Processes and considerations—with emphasis on northern environments. *Can Tech. Rep. Fish Aquat. Sci.* **2009**, 2826. Available online: https://www.researchgate.net/publication/236688246_Creating_lakes_from_open_pit_mines_processes_and_considerations_with_emphasis_on_northern_environments_Canadian_Technical_Report_of_Fisheries_and_Aquatic_Sciences (accessed on 12 January 2021).
2. Eary, L.E. Geochemical and equilibrium trends in mine pit lakes. *Appl. Geoch.* **1999**, *14*, 963–987. [CrossRef]
3. Castro, J.M.; Moore, J.N. Pit lakes: Their characteristics and the potential for their remediation. *Environ. Geol.* **2000**, *39*, 1254–1260. [CrossRef]
4. Gammons, C.H.; Duaime, T.E. Long term changes in the limnology and geochemistry of the Berkeley Pit Lake, Butte, Montana. *Mine Water Environ.* **2006**, *25*, 76–85. [CrossRef]
5. Schultze, M.; Pokrandt, K.-H.; Hille, W. Pit lakes of the Central German lignite mining district: Creation morphometry and water quality aspects. *Limnologica* **2010**, *40*, 148–155. [CrossRef]
6. Geller, W.; Schultze, M.; Kleinmann, R.; Wolkersdorfer, C. (Eds.) *Acidic Pit Lakes*; Springer: Berlin/Heidelberg, Germany, 2013; p. 525.
7. Żurek, R. Lakes in large scale open-pits in Poland. In *Acidic Pit Lakes*; Geller, W., Schultze, M., Kleinmann, R., Wolkersdorfer, C., Eds.; Springer: Berlin/Heidelberg, Germany, 2013; pp. 291–315.
8. McCullough, C.D.; Vandenberg, J. Studying mine pit lake systems across multiple scales. *Poland. Mine Water Environ.* **2020**, *39*, 173–194. [CrossRef]

9. Blanchette, M.L.; Lund, M.A. Foreword to Special Issue on Pit Lakes: The Current State of Pit Lake Science. *Mine Wat. Environ.* **2020**, *39*, 425–426. [CrossRef]
10. Shevenell, L.; Connors, K.A.; Henry, C.D. Controls on pit lake water quality at sixteen open-pit mines in Nevada. *Appl. Geoch.* **1999**, *14*, 669–687. [CrossRef]
11. Castendyk, D.N.; Eary, L.E.; Balistrieri, L.S. Modeling and management of pit lakes water chemistry 1: Theory. *Appl. Geoch.* **2015**, *57*, 267–288. [CrossRef]
12. Boehrer, B.; Kiwel, U.; Rahn, K.; Schultze, M. Chemocline erosion and its conservation by freshwater introduction to meromictic salt lakes. *Limnologica* **2014**, *44*, 81–89. [CrossRef]
13. Molenda, T. Conditions for development of anthropogenic meromictic reservoirs in the workings of crystalline rocks (based on the examples of the quarries of the Žulovská pahorkatina, NE Czech Republic). *Environ. Earth Sci.* **2015**, *74*, 2259–2271. [CrossRef]
14. Pellicori, D.A.; Gammons, C.H.; Poulsen, S.R. Geochemistry and stable isotope composition of the Berkeley pit lake and surrounding mine waters, Butte, Montana. *Appl. Geoch.* **2005**, *20*, 2116–2137. [CrossRef]
15. Bromowicz, J.; Magiera, J. Stones used in early medieval Krakow buildings. Geological and mining issues. *Górn. Odkr.* **2008**, *49*, 62–71. (In Polish)
16. Sermet, E.; Rolka, G. Pogórniczy spadek na zrębie Zakrzówka. In *Dzieje Górnictwa-Element Europejskiego Dziedzictwa Kultury*; Zagożdżon, P., Madziarz, M., Eds.; Oficyna Wydawnicza Politechniki Wrocławskiej: Wrocław, Poland, 2013; Volume 5, pp. 329–338.
17. Iwanoff, A. Environmental impacts of deep opencast limestone mines: In Laegerdorf, Northern Germany. *Mine Wat. Environ.* **1998**, *17*, 52–61. [CrossRef]
18. Robles-Arenas, V.M.; Candela, L. Hydrological conceptual model characterisation of an abandoned mine site in semiarid climate. The Sierra de Cartagena-La Unión (SE Spain). *Geol. Acta* **2010**, *8*, 235–248.
19. Molenda, T. Impact of saline mine water discharge on the development of meromictic pond, the Rontok Wielki reservoir, Poland. *Mine Wat. Environ.* **2018**, *37*, 807–814. [CrossRef]
20. Matyszkiewicz, J. Epigenetic silification of the Upper Oxfordian limestones in the vicinity of Kraków. *Ann. Societ. Geol. Pol.* **1987**, *57*, 59–87. (In Polish)
21. Krajewski, M. Upper Jurassic chalky limestones in the Zakrzówek Horst, Kraków-Wieluń Upland (South Poland). *Ann. Societ. Geol. Pol.* **2001**, *71*, 43–51.
22. Krajewski, M.; Bajda, T. Mineralogical and geochemical diversification of Upper Jurassic limestones of Zakrzówek Horst, Kraków region, Southern Poland. *Kwart AGH Geol.* **2002**, *28*, 129–143. (In Polish)
23. Gradziński, R. Origin and development of subterranean karst in the Southern part of the Cracow Upland. *Rocz. Pols. Tow. Geol.* **1962**, *32*, 429–493. (In Polish)
24. Gradziński, R. Geological Map of Kraków Region. Institute of Geological Sciences, Polish Academy of Sciences. 2009. Available online: https://www.ing.pan.pl/en/geological-museum/geological-map-of-the-krakow-area (accessed on 12 January 2021).
25. Motyka, J.; Postawa, A. Influence of contaminated Vistula River water on the groundwater entering the Zakrzówek limestone quarry, Cracow region, Poland. *Environ. Geol.* **2000**, *39*, 398–404. [CrossRef]
26. Dodds, W.K.; Whiles, M.R. Freshwater Ecology. In *Concepts and Environmental Applications of Limnology*, 2nd ed.; Elsevier: Amsterdam, The Netherlands, 2010; p. 811.
27. Younger, P.L.; Banwart, S.A.; Hedin, R.S. Mine Water. Hydrology, Pollution, Remediation. *Kluwer Acad. Publ.* **2002**, *32*, 739.
28. Motyka, J.; Postawa, A. The groundwater of Zakrzówek horst (S Kraków-Czestochowa Upland). *Biul. PIG* **2004**, *412*, 71–130. (In Polish)
29. Motyka, J.; Czop, M. Water quality changes in the abandoned Zakrzówek limestone quarry near Cracow (Poland). *Pol. J. Environ. Stud.* **2004**, *13* (Suppl. S3), 187–191.
30. Bethke, C.M.; Yeakel, S. *The Geochemist's Workbench ®Release11–GWB Essentials Guide*; Aqueous Solutions LLC: Champaign, IL, USA, 2018.
31. Golterman, H.L. Physiological Limnology. An Approach to the Physiology of Lake Ecosystems. Develop. *Water Sci.* **1975**, *2*, 489.
32. Galas, J. Limnological study on a lake formed in a limestone quarry (Kraków, Poland). I. Water chemistry. *Pol. J. Environ. Stud.* **2003**, *12*, 297–300.
33. Malata, M.; Motyka, J.; d'Obyrn, K.; Postawa, A. Chemistry of water in the gypsum pit lake Gacki (Nida Basin, SE Poland). *Górn. Odkrywk.* **2018**, *2*, 43–49. (In Polish)
34. Różkowski, J. Transformations in chemical composition of karst water in the southern part of the Cracow Upland (Rudawa and Prądnik drainage areas). *Kras Speleol.* **1996**, *1*, 106. (In Polish)
35. Żurek, A.; Czop, M.; Motyka, J. Nitrate in groundwater of the Jurassic aquifer in Olkusz region (southern Poland). *Kwart. AGH Geol.* **2010**, *36*, 423–434. (In Polish)
36. Fabri, E.S.; Carneiro, M.A.; Praça Leite, M.G. Hydrogeochemical characteristics of pit lakes formed in abandoned ornamental rocks quarries of Campo Belo Metamorphic Complex, Minas Gerais, Brazil. *Manag. Env. Qual. Intern. J.* **2012**, *24*, 82–93. [CrossRef]
37. Czop, M.; Motyka, J.; Sracek, O.; Szuwarzynski, M. Geochemistry of the hyperalkaline Gorka Pit-Lake (pH > 13) in the Chrzanow Region. *South. Pol. Water Air Soil Pollut.* **2011**, *214*, 423–434. [CrossRef]

38. Sracek, O.; Berg, M.; Müller, B. Redox buffering and de-coupling of arsenic and iron in reducing aquifers across the Red River Delta, Vietnam, and conceptual model of de-coupling processes. *Environ. Sci. Pollut. Res.* **2018**, *25*, 15954–15961. [CrossRef] [PubMed]
39. Appelo, C.A.J.; Postma, D. *Geochemistry, Groundwater and Pollution*, 2nd ed.; CRC Press: Boca Raton, FL, USA, 2005.
40. Motyka, J.; Czop, M. Vertical changes of iron and manganese concentration in water from abandoned Zakrzówek limestones quarry near Cracow. In Proceedings of the 10th IMWA Congress: Mine Water and the Environment; Rapantova, N., Hrkal, Z., Eds.; IMWA: Karlovy Vary, Czech Republic, 2008; pp. 559–562.
41. Couture, R.M.; Gobeil, C.; Tessier, A. Arsenic, iron and sulfur diagenesis in lake sediments. *Geoch. Cosmog. Acta* **2010**, *74*, 1238–1255. [CrossRef]
42. Azizi, F.; Vadiati, M.; Asghari Moghaddam, A.; Nazemi, A.; Adamowski, J. A hydrogeological-based multi-criteria method for assessing the vulnerability of coastal aquifers to saltwater intrusion. *Environ. Earth* **2019**, *78*, 1–22. [CrossRef]
43. Güler, C.; Kurt, M.A.; Alpaslan, M.; Akbulut, C. Assessment of the impact of anthropogenic activities on the groundwater hydrology and chemistry in Tarsus coastal plain (Mersin, SE Turkey) using fuzzy clustering, multivariate statistics and GIS techniques. *J. Hydrol.* **2012**, *414*, 435–451. [CrossRef]
44. Eskandari, E.; Mohammadzadeh, H.; Nassery, H.; Vadiati, M.; Zadeh, A.M.; Kisi, O. Delineation of isotopic and hydrochemical evolution of karstic aquifers with different cluster-based (HCA, KM, FCM and GKM) methods. *J. Hydrol.* **2022**, *609*, 127706. [CrossRef]
45. Khosravi, R.; Zarei, M.; Sracek, O. Hydraulic and geochemical interactions between surface water and sediment pore water in seasonal hypersaline Maharlu Lake, Iran. *Hydrol. Processes* **2020**, *34*, 3358–3369. [CrossRef]