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Geological outline of sulphur beds in Poland and Ukraine

In Europe, large deposits of sulphur were formed on the border of the Carpathian Foredeep and the continental East European Platform. The Foredeep has a length of 1700 km (300 km in Ukraine), and a width of 5 - 75 km. The elevation of the terrains is 230 - 270 m asl and is filled by sedimentary materials including dolomite, salt, gypsum, phosphorite and sulphur. Most of the deposits of native sulphur are a product of sulphate reduction with hydrocarbons and bacteria participation.

Deposits of sulphur in Poland were discovered in the 1950s. Almost simultaneously, sulphur was also discovered in Ukraine not far from Poland. Later, in the 1960s, these deposits were exploited both by underground mining, opencast mining and underground melting (the Frasch method). These sites are shown in Figure 1. Opencast technology was used in four mines in Ukraine and two in Poland. Almost all the mines in the pre-Carpathian sulphur-bearing basin were closed in the 1990s due to non-profitable exploitation. All these pits are now more or less flooded. Reclamation treatments are in various states of advancement.

Origin of native sulphur. Native sulphur occurs in products of volcanic exhalation in the craters of dormant volcanoes. It can be formed by sedimentary processes. The main part of the sulphur arises in a gypsum reduction process which takes place during microbiological processes. These kinds of deposits have industrial importance. Two types of deposits are distinguished into, firstly, a Sicilian type in which sulphur-bearing marl layers are syngenetic with remaining sediments and secondly, a Louisiana type where sulphur-bearing limestone arises epigenetically (secondary). The Sicilian types of deposit are evidently related to primary sedimentary reservoirs. All the beds of native

sulphur in marginal parts of the Carpathian Foredeep belong to strata beds of the Sicilian type, (Nieć, 1986). This Pre-Carpathian sulphur-bearing basin is one of the largest in Eurasia. Documented reserves of native sulphur in the Carpathian Foredeep are of up to 300 m in depth. This has been shown for thirteen beds which comprise 467.8 million tons and a further 121 million tons is contained in protecting pillars (Przeniosło, 2005). The main mineral component of sulphur-bearing limestone is calcite (average ca. 62%) and native sulphur (on an average 35%).The remaining portion of ore consists of locally abundant clay minerals, gypsum, celestine, pyrite, barite and admixtures of gypsum, quartz and accessory minerals (strontianite, witherite).

The Polish and Ukrainian sulphur beds are classed as being of biogenic origin. Up to now a bioepigenetic origin of native sulphur has been accepted (i.e. sulphur created due to microbial reduction of gypsum in the presence of hydrocarbons under a hermetic cover of cap-rock), (Kubica, 1997; Pawłowski et al. 1979).

This opinion gives rise to many doubts and is questionable. New geological facts (Gąsiewicz 1994, 2000a, 2000b) indicate an evidently sedimentary genesis of this limestone and thereby syngenesis of miocenic beds of native sulphur in Poland. The presence in sulphur-bearing limestones of evident relicts of primary crystals of scienitic gypsum, so called post-selenitic limestone – is the key evidence of epigenesis. There is no analogy in the formation of the surrounding gypsum (Nieć 1982). Some other geologists believe that karstification is one of the most important processes controlling the formation of sulphur deposits in Pre-Carpathian region (Klimchouk, 1997).

Some important industrial deposits of sulphur minerals belong to hydrothermal formations of pyrite and copper. Plutonic hydrothermal

formation arises from impregnation of siliceous rock. These deposits deliver around 35% of the world production of sulphur.

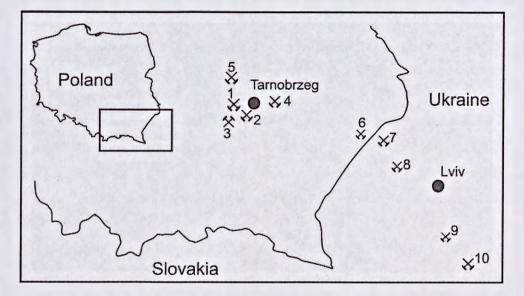


Figure 1. Location of sulphur mining in Poland and Ukraine. Flooded: 1 – Piaseczno; 2 – Machów; 8 – Yavoriv; 9 – Rozdol; 10 – Podorozhne. Underground melting: 3 – Osiek; 4 – Jeziorko; 5 – Grzybów; 6 – Basznia (Bashnia); 7 – Ncmyriv.

Characteristic of Polish and Ukrainian flooded sulphur pits

Yavoriv. The ledge has two fields, Main and Pivdienne, at a depth of 46 m. The main field had a sulphur reserve of 67 million tons. This field was exploited by underground mining between 1983 and 2006. Field Pivdienne had a sulphur reserve of 15 million tons at a depth of 120 m. This deposit was exploited from 1974 to 1993 by the Frasch method and later by opencast mining. The output

was 6.5 million tons, i.e. 43 % of the resources. When Pivdienne closed, it was partially filled with mining waste. Six pumps were employed to remove 1200 to 2000 m³ h⁻¹ of water into the Horodnica Stream. In 2001 the pumps were turned off and flooding began. The mine was flooded 'as is' using water from the Szkło River (the annual input is 37×10^6 m³ of river water and 3.6×10^6 m³ of underground water). Outcrops of sulphur limestone were not isolated from the water. Flooding continued until December 2006. The depth of the resulting water body is 70 m, the area of the water table is 932 ha at 231 m asl. The volume of the opencast part is 402×10^6 m³, and the volume of the inner dump is 97×10^6 m³, with a designed volume of water of 230×10^6 m³, and an actual volume of 205 x 10^6 m³. There is a 790-ha bird reserve (Tsholgini) on the dumping ground.

Niemirov. The Niemirov ledge passes on the Polish side. The Ukrainian east field reaches to a depth of 19 - 60 m, and the western field to 200-320 m. The western field was exploited by the Frasch method in mines Zavadivska and Shavarivska. Exploitation of the Grushevske field closed after nine months due to low efficiency. In the vicinity of the mine approximately 100 incidents of subsidence were recorded.

Rozdol. This mine was exploited between 1956 and 1992 and was then backfilled and divided into three lakes in a cascade: Czyste (area 10 ha, depth 15 m, pH ca. 8, SO₄ ca. 1250 mg L⁻¹), Srednie (area 45 ha, depth 12 m, pH ca. 6, SO₄ ca. 2000 mg L⁻¹), and Glubokoe (area 82 ha, depth 40 m, pH 7.2, SO₄ ca 1600 mg L⁻¹). The area was flooded by surface water (1.1 x 10^6 m³ y⁻¹) and underground water (0.45 x 10^6 m³ y⁻¹). A channel discharged the overflow into the Dniestr River. Reclamation is now complete.

Podorozhne This mine was exploited between 1971 and 1997. The opencast was then abandoned and not reclaimed. It is 4 km long, 1.8 km wide, has an area of 420 ha, a depth of 90 m and a volume of 124×10^6 m³ (Gaydin & Zozulja 2004; Gaydin & Zozulja 2007).

Piaseczno. [Piasetschno] The present area of this mine is 63 ha, with a depth of 22 m. After forming the bowl of the reservoir, the area attained will be 160 ha with a depth of 42m and a volume of $27 \times 10^6 \text{ m}^3$. Only the outcrops above the water table have been isolated (between 122 and 146 m asl); outcrops below the water table (down to 100 m asl) remain unisolated. The predicted time for autogenous filling is 6–7 years (Figure 2).

Machów. The sulphur was exploited between 1969 and 1992. The mine was then backfilled with shale and silt from the inner dumping ground. Below the isolating layer is 3.74×10^6 tons of industrial waste.

The depth of the mine during active work reached 110 m, but was later backfilled to a depth of 45m. Flooding began in spring 2005 using water from the Vistula River, and is completed in spring 2009. The reservoir have an area of 560 ha and a volume of $112 \times 10^{\circ}$ m³. The external dumping ground has an area of 880 ha and a height of 60 m. There are seven small lakes with surface area of 0.1 to 3.5 ha and a depth of 1.5 to 14 m. The inner dumping ground has an area of 720 ha. Depth of opencast was 70 - 110 m.

Topography and chemical properties of the Piaseczno opencast mine.

The Piaseczno opencast mine is located at 50° 33.08'N, 21° 36.01'E. Sulphur was mined until 1971 and then 5 million tons of sand was excavated as a reserve for the glass industry.

In 1980 exploitation was finished and the pit began to fill up with water. Pumps were installed at mid depth at 123 m asl (Figures 2 and 3). After inundation the water table was kept at 121 - 122 m asl. The depth of the reservoir is 21 - 22 m.

Due to the hydraulic connection with the adjoining opencast mine Machów and reclamation works, this level is still maintained today.

| Opencast name | Location | Underground melting mine | Location |
|---|--------------|--------------------------|--------------------------------|
| Piaseczno Sulphur 1958-1971 Sand 1971-1980 | 50°33'06"N, | X Osiek | 50° 30'18"N, |
| | 21°35'33"E | 1993→ | 21° 26'13"E |
| Machów 1969-1992 | 50°32'22" | N, X Jeziorko | 50° 34'05"N, |
| | 21°38'40"E | 1967-2001 | 21°50'E |
| ¥ Yavoriv | 49° 55 15"N, | × Basznia | 50°09'24"N, |
| 1974-1993 | 23°26'E | 1977- 1993 | 23°16'05"E |
| × Nowy Rozdil | 49°27'49"N, | X Grzybów 1966-1996 | 50°32'40"N, |
| 1958-1992 | 24°05'20"E | | 21°02'30"E |
| Podorozhne 1978-1994 | 49°14'50"N, | Nemiriv | 50°04'17"N, 23° |
| | 24°11'E | 1980-1992 | 32'E |
| | | X Machów II 1985-1993 | 50° 32' 22" N, 21° 38' 40"E |

Table 1. List of flooded (partially and completely) sulphur pit mines andFrasch mines in Poland and Ukraine.

The pit was inundated by tertiary and quaternary water in different proportions. As the water level increased, the fraction of tertiary water decreased. Tertiary water is relatively strongly mineralised, with a mean solute concentration of 2170 mg L^{-1} . The mineralisation of the same kind of water in Ukraine is double that (Table 1). The type of water from both from the tertiary and quaternary aquifer can be named in the Altovski-Shvec classification (Macioszczyk 1987) as

the sulphate-chloride-sodium-calcium (SO₄-Cl-Na-Ca) type. Compared to Ukrainian post-sulphur mining reservoirs, the water in Piaseczno has the lowest total dissolved solids (TDS) amount (Table 2).

Table 2. Comparison of Neogenic water of Polish and Ukrainian mines. (Gaydin2000; Frankiewicz & Pucek 2006; Kirejczyk et al. 2007; Żurek 2007).

| Mine | рН | H_2S | Са | Mg | Na+ K | SO4 | HC O ₃ | C1 | Sum |
|---------------------------------|-------------|---|---------|------|----------|------|----------------------|-----|--------|
| | | | | | mg L | -1 | | | |
| Podorozhna | 7.6 | 25 | 455 | 84 | 772 | 3260 | 451 | 100 | 5450 |
| Rozdol | 6.7 | 39 | 561 | 53.5 | 210 | 1565 | 646 | 6.2 | 3060 |
| Yavoriv | 6.8 | 47 | 556 | 62 | 210 | 1600 | 476 | 35 | 2700 |
| Piaseczno | 6.5- | 6.1 | 280 | 34 | 340 | 770 | 370 | 370 | 2170 |
| Tertiary water | 7.0 | | | | | | | | |
| Piaseczno Qua- ternary water | 6.8- 7.2 | - | 362 | 59 | 130 | 1100 | 324 | 143 | 2190 |
| Rain-water | 3.7- 5.0 | | 2 | | 2.5 | 10 | | | ca. 20 |
| | FOL | AND 373.8 ma.l. 2735 E 2735 E 2735 E 1000000 A 1000000 A 1000000000000000000000000000000000000 | - Puton | | | | 10m 3 | | |

Figure 2. The contemporary water table of the Piaseczno reservoir; 1. The horizontal extent of Tertiary formations (Krakoviec clays, gypsum, sulphur-bearing limestone) 2. The horizontal extent of Quaternary formations, 3. The designed final water table in the opencast mine; A—B: line of geological cross-section.

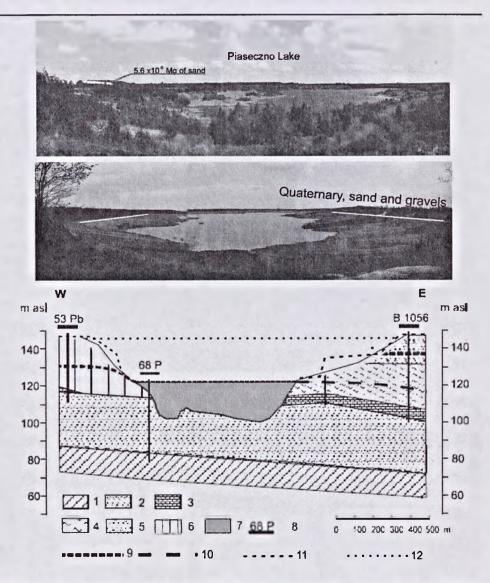


Figure 3. Geological cross-section of the Piaseczno opencast mine: 1. Cambrian shale; 2. Tortonian, sands and sandstones; 3. Torton, chemical series, sulphurbearing limestone, barren limestone and gypsum; 4. Sarmatian, Krakoviec clays; 5. Quaternary, sand and gravels; 6. inner waste bank – sands, gravels, clays, silts; 7. Present water level of Piaseczno reservoir; 8. Documented geological exploratory bore-holes; 9. Water table of Quaternary aquifer; 10. Potential surface of Tertiary aquifer; 11. Old bowl profile; 12. Future water level. Above: Profiling of bowl reservoir in 2008 and view before 2008.

The specific geological situation (Figure 3) determines the chemical and physical properties of water. As in each opencast mine, draining of inflowing water bares outcrops and brings specific sets of elements in. Sulphur-bearing limestone and sedimentary rocks are rich in calcium, carbonate and sulphate. These rocks of marine origin have also raised concentrations of Na, Cl, Br, J and relatively low amounts of heavy metals. The discrimination technique distinguished three chemically different layers (Żurek 2006a): the upper layer, \pm equal to the photic zone; the transitional layer in the dark hypolimnion; and the monimolimnetic layer below the chemocline, (Figure 4). The first two layers are chemically similar and mathematical analysis techniques partially overlay them. The Piper's diagram (Fig. 4) confirms these three layers. All techniques of chemical classification based on ion proportions are imperfect. They do not take into account the biological or chemical processes which are necessary for detailed characterisation.

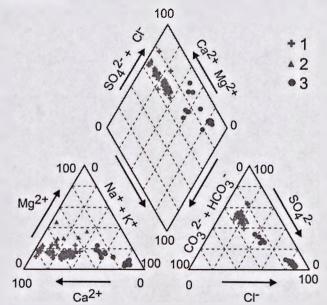


Figure 4. Diagram of water chemistry for three layers. 1 - samples from depth 0, 2.5, 5, 7.5 m; 2 - samples from 10 and 15 m; 3 - samples from 20 m.

The upper 0.5 m layer is usually diluted by rainwater. Total dissolved solids in this superficial layer is *c*. 1000 mg L⁻¹; deeper layers have a greater content of solute, *c*. 2000 mg; and in the monimolimnion, the content of TDS increases to *c*. 10 000 mg L⁻¹. The concentration and relations between main ions (Ca²⁺, Mg²⁺, Na⁺, Cl⁻, HCO₃⁻, SO₄²⁻) and the products of their transformations delimit boundary conditions of life and often decide about lake type. This set of basic ions is quite different from that found in acid reservoirs (see Section 5.1.2.), however both are meromictic. Contrary to acid reservoirs, which are rich in iron compounds, the transformation of sulphates and carbonates in these postsulphur mines are most important. The reaction of water in the photic zone is alkaline but rarely >8.0. In the deep layers, pH is *c*. 7.0 – 7.3 (Table 3).

| Table 3. Concentrations | of main el | ements and | anions | [mg L | ']. |
|-------------------------|------------|------------|--------|-------|-----|
|-------------------------|------------|------------|--------|-------|-----|

| Layer | pН | Ca | Mg | Na | K | C1 | SO4 | H_2S/HS^- |
|---------------|------|------|-----|-------|-----|-------|------|-------------|
| mixolimnion | 6.9- | 153- | 29- | 14- | 5- | 125- | 326- | 0 – |
| | 8.6 | 518 | 190 | 290 | 13 | 412 | 1027 | 4.2 |
| monimolimnion | 7.4- | 318- | 76- | 6900- | 13- | 1120- | 215- | 0.5- |
| | 7.8 | 590 | 228 | 10045 | 280 | 5000 | 994 | 4.3 |

The presence of native sulphur and gypsum in outcrops as well as sulphate in the water implies intensive biological and chemical sulphur

transformations. Beyond the light range, reductive processes begin. Sulphate is reduced to very reactive hydrogen sulphide. This reaction is reversible. At a depth of 10-15 m, oxidizing H_2S to SO_4 can by locally very intensive. When the concentration of sulphate (mainly as $CaSO_4$, less as MgSO₄, comp. Table 3) is greater then its solubility, the surplus is precipitated and water becomes turbid. This phenomenon was observed in the examined reservoir. Simultaneously with SO₄ transformations, Fe, Mn, Zn transformation occurs.

Biogenic elements

The photic layer is poor in nitrate, usually with concentrations below 0.5 mg N–NO₃ L^{-1} . In the lower part of the hypolimnion and monimolimnion, this form is often absent. In contrast, ammonium is present in low concentrations in the photic zone, but rapidly increases with depth up to 25 mg L⁻¹ N–NH₄ in the anoxic zone. Concentrations of PO₄ are highest in the surface layer at 0.2 to 0.25 mg L⁻¹, while medium values of 0.1 mg L⁻¹ occur in the lower epi-, meta- and upper hypolimnion. Below this layer, concentrations decrease to 0.05 mg L⁻¹. According to nutrient concentration criteria, P content indicates a hypereutrophic state (0.096-0.384 mg L⁻¹, Carlson 1977). Meanwhile, the reservoir is oligotrophic.

Trace elements in water

The concentration of Cd in the water column ranged from 0.21–43.0 μ g L⁻¹; Pb from 0.5–183.3 μ g L⁻¹; Cu from 0.5–59.5 μ g L⁻¹; Zn from 2.5–40.2 μ g L⁻¹; Mn from 0.27–8.35 μ g L⁻¹; Fe from 0.05–57.4 μ g L⁻¹; and Sr from 1.2–29.5 μ g L⁻¹. In general, the concentration of Zn in the water was low, that of Cd, Pb, Cu, Mn

and Fe ranged from relatively low to very high, whereas that of Sr was very high compared with unpolluted regions. Vertical distribution profiles are characteristic for some elements. Zn has low concentrations in the katalimnion (depth *c*. 12 m), whereas near the surface and the bottom, concentrations are greater. This suggests a precipitation process under anoxic conditions – the reduction of SO_4^{2-} to H_2S/HS^- following organic matter mineralisation by bacteria, which leads to the formation of metal sulphides such as ZnS.

Concentrations of Fe and Mn are the highest in the zone of reduction/ oxidizing, i.e. in the katalimnion (Szarek-Gwiazda & Żurek 2006). In the mixolimnion, the concentration of these metals is 100 times lower. All trace metals have higher concentrations in the monimolimniom.

Element speciation

A six step sequential extraction procedure was applied to determine operationally defined phases: exchangeable (F1), carbonate (F2), easy reducible (F3), moderately reducible (F4), organic/sulphides (F5) and residual (F6) in sediment. Differences in trace element (except Mn) speciation in the littoral sediment with respect to lake depth was not found. A great part of Pb, Mn and Fe in the anoxic sediment was found in moderately reducible phase. It was probably caused by the extremely high Fe content both in the monimolimnion water (up to 45 mg L^{-1}) and in the upper layer (0–15cm) of profundal sediment (32.4% dry mass). Considerable differences in the trace element speciation between the littoral sediment and permanently anoxic profundal sediment were found.

Cd was a mobile element in the littoral sediment. Most of Cd (58.2-43.6%) is bound to carbonates at depths of 1 to 10 m. 26% of Cd was bound to F6 (metals largely embedded in the crystal lattice of sediment fraction and is relatively stable in the natural sediment environment). It is different pattern of Cd association

than found in other lakes – there Cd is usually bound with organic matter or hydrated iron and manganese oxides.

Pb. The pattern of binding forms in sediment was similar independent of depth. Around 50% of the Pb is bound to immobile (F6) fraction. Fractions of F2, F3 and F4 contain 14-18% of Pb.

Cu. This element is associated with immobile F4 and F6 in the littoral. These two fractions have 38% at 1 m to 47% at 10 m. Only 1.5% Cu was bound with the most mobile F1 fraction at all littoral stations. Contrary to other lakes, small amount of Cu is associated with the organic/sulphide fraction in the littoral sediment of Piaseczno Lake. This can be explained by the oligotrophic character of the lake and the small amount of organic matter in the sediment.

Mn is associated mainly with F2, F3 and F4 fractions. Much smaller amounts of Mn were associated with exchangeable fractions, organic/sulphide fractions and residual fractions. Mn was most mobile at 1m. Mobile fractions F1, F2 and F3 were made up ca. 77% of Mn. Its mobility lowered with lake depth. At the deeper stations at 5 and 10 m these fractions were made up of 63 and 55% Mn respectively.

Fe was a rather immobile element. At all depths, most of the Fe was bound in fractions F4 (54%) and F6 – 32-37%. Less than 0.1% of Fe was in mobile fraction F1.

Carbonates played an important role in the accumulation of Ca, Cu, Mn and Fe in the anoxic sediment. Also an organic/sulphide phase has played an important role in Cd, Cu, Mn and Fe binding in the sediment.

Heavy metals and fishes

Like other chemical compounds, heavy metals are assimilated and excreted by living organisms. Fishes are convenient organisms to trace the assimilation and location of elements in their organs. The distribution of heavy metals was examined in some fish species from the Piaseczno lake (Szarek-Gwiazda & Amirowicz 2006).

The content of Cu in fish tissues (except gills) was relatively low. The content of copper in the gills of all the studied species was very high. The concentrations of Mn and Fe in the liver, kidney and gills, and of Sr mainly in the gills were much higher than those determined in other waters. In general, all the correlations between fish length, weight, age and trace element concentration in the studied tissues of roach and perch were very weak. In general, the patterns of element bioconcentration in fish tissues (G, gills; K, kidney; L, liver) of studied species were as follows:

Cd: roach (K)>silver bream (K)>perch (K)>rudd (L)

Pb: roach (K)>silver bream (K)>perch (K)>rudd (K)

Cu: rudd (G)>roach (L)>silver bream (L)>perch (K)

Mn: silver bream (G)>rudd (G), roach (G)>perch (G)

Fe: perch (K)>roach (L)>rudd (G)>silver bream (G)

Sr: silver bream (G)>rudd (G)>roach (G)>perch (G)

In general, the species which find a large portion of their food by burrowing in the bottom substrate (i.e. roach and silver bream) achieved higher ranks in the above patterns than those which forage mainly in the macrophyte beds or are predatory (rudd and perch).

Bottom sediments

Bottom sediments have two layers: the upper 3 -10 cm is formed by black sulfides, and deeper layer is formed by grey silt from eroded banks. Generally, the concentration of the major elements (N, P, S, Ca, K, Mg, Cl, Fe, Si and Al) and trace elements (Ag, As, Ba, Cd, Co, Cr, Cu, Ga, Hg, I, Mn, Mo, Ni, Pb, Rb, Sr, Ti, Y and Zn) in the lake sediment reflected the natural regional background

(Table 4). The sediment has a primarily mineral character with small amounts of organic matter. The concentrations of some major and trace elements differed according to the studied transects, depths and season. The lowest concentrations of the studied elements were found at a depth of 1 m. Generally, the results show a substantial chemical heterogeneity of the bottom sediment, which is probably connected with its allochthonous origin and also with the young age of the lake. Concentration of some trace elements are constant during the year like Sr ($323 - 567 \ \mu g \ g^{-1}$), Fe (21.7 - 24.3), Mn (3.5 - 8.2), Cu (40 - 46) Pb (22.1 - 25.4) were seasonally very variable like Cd ($0.27 - 2.1 \ \mu g \ g^{-1} \ dry \ mass$).

Genesis of meromixis.

Hakala (2004) estimates that in Finland, one lake in 800 is meromictic. Meromixis can resulted from a) flow/precipitation of saline water over freshwater or freshwater over saline water, b) superficial diffuse nutrient load and/or turbidity currents from the catchment, c) subsurface inflow of groundwater, and d) inadequate mixing due to the lake morphology and surrounding topography. Due to genesis, Boehrer and Schulze (2006) distinguish a few types of meromixis: ectogenic, biogenic and crenogenic. The Piaseczno reservoir indicates a crenogenic origin of meromixis. Infiltering tertiary salty water uncovered limestone deposits, which were covered by floating fresh water from quaternary alluvia and precipitation. 28 % of inflowing water originates from the Vistula River and has a concentration of 100 to 300 mg L⁻¹ Cl⁻ (Żurek & Kasza 2002). In fact, in the epilimnion, concentrations of the Cl-marker are comparative at *c*. 200 mg L⁻³. The morphology and depression of the pit (-30 m below the surrounding terrain) is conducive to a meromixic state. In the future, after the reservoir is full, the inflow of tertiary water will diminish (see Table 6). A new strati-

| Table 4. Mcan chemical composition (as %) of the sediments of the Piaseczno reservoir. Trace elements as $\mu g g^{-1}$ o sediment dry mass. Acc. to Szarek-Gwiazda et al. (2006). | f. | |
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| | | | | | 2 | Macroelements | nents | | | | | | |
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| | N tot | Piot | S 101 | Piot Siot Ca Mg K | Mg | 1.00 | CI | Fe | Cl Fe Mn Si Al | Si | AI | | |
| Sediment | 0.040 | 0 00 6 | 7.6 | 5.6 | 1.1 | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | 0.7 | 2.4 | 0.5 | 46.4 | 4 | | |
| | | | | | | Trace elements | nents | | | | | | |
| | Pb | Cu | Zn | Cu Zn Cr Ni Sr | Ni | Sr | Mo | Rb | Mo Rb Ba Ga Y Ti | Ga | Y | Ξ | J |
| Sediment | 23,4 | 43.8 | 72.0 | 113.0 | 32.3 | 43.8 72.0 113.0 32.3 453.0 76.8 64.3 554.4 14.6 65.3 4.8 | 76.8 | 64.3 | 554.4 | 14.6 | 65.3 | | 178.3 |
| Reference rock: silt denosits | 34.0 | 25.8 | 19.3 | 43.7 | 35.3 | 25.8 19.3 43.7 35.3 134.7 24.3 34.2 92.3 33.8 25.5 48.7 139 | 24.3 | 34.2 | 92.3 | 33.8 | 25.5 | 48.7 | 139 |

fication will be established, but there is a high probability that the reservoir will remain meromictic.

Bacterioplankton

The bacterial profile in post sulphur mining reservoirs is complex. The euphotic zone is usually neutral or weakly acid occupied by and bacteria Metallogenium, which are Fe²⁺ oxidizing at c. neutral pH. In the cyanobacteria same layer, Oscillatoria prolifica (Greville) Gomont can be found. At a depth of 5-10 m, Thiobacillus sp. (also known as Acidithiobacillus) can be found. Some species of this genus are acidophilic, whereas a few species only grow at neutral pH. On the border of the photic zone can be found some species of

cyanobacteria or *Chlorobiaceae*. When hydrogen sulphide is present and sufficient illumination is available, purple as well as green sulphur bacteria like *Chromatium* and *Chlorobium* start primary production through anoxygenic photosynthesis. In the hypolimnion live *Siderocapsa, Spirothrix*. Numerous filaments of *Beggiatoa* sp. were observed in the monimolimnion of Piaseczno. Different species are able to participate in the same process, substituting one for another. Therefore, this scheme may be different from one reservoir to another, but generally, the microbiological processes in all post-sulphur mines are similar.

These bacteria have either gas vacuoles or flagella so that they can be maintained just below the metalimnion to trap any available light. Gas vacuole-containing bacteria occurring in this region include *Amoebobacter*; *Lamprocystis, Thiopedia, Thiodictyon* and *Ancalochloris*.

Bacterial activity, case of Piaseczno reservoir. Respirometric measurements of microbial activity in the mixolimnion measured as oxygen consumption are 0.1 to 2.0 mg L⁻¹ d⁻¹ and emissions of CO₂ were 1.5–46.6 mg L⁻¹ d⁻¹. In the monimolimnion, CO₂ production was 3 - 5 time greater than in the mixolimnion. In fact, this observation is consistent with the CO₂ concentrations: 100 – 200 mg L⁻¹ in the monimolimnion versus 5 – 30 in the mixolimnion (Table 5). The presence of large sulphur bacteria (*Beggiatoa*) was very considerable in the monimolimnion, i.e. below 20 m, (Bucka & Wilk-Woźniak 2005).

Table 5. Oxygen consumption and CO₂ production in different layers of reservoir Piaseczno, (Mazurkiewicz unpubl.)

| | Mixolimnio | n | Monimolim | nion |
|---|--|---|--|---|
| | summer | winter | summer | winter |
| Oxygen consumption rate $(mg O_2 L^{-1} h^{-1})$ Carbon dioxide release rate $(mg CO_2 L^{-1} h^{-1})$ Bacterial biomass (mg C $L^{-1})$ Chlorophyll a (mg L ⁻¹) | 0.09-0.14 0.04-2.8 0.007- 0.095 0.74-5.9 | 0.17-0.33 0.11-0.92 0.004-0.1 0.3-0.32 | 0.07-0.36 0.9-2.18 0.185-0.26 - | 0.07-0.4 1.4-3.16 0.005- 0.015 |

Bacterial activity, case of Yavoriv reservoir. Kit et al. (2004) isolated purple sulphur bacteria *Thiocapsa roseopersicina* and *Lamprocystis roseopersicina* from the Yavoriv reservoir. They found that these bacteria are able to assimilate simple organic compounds like glucose, rhamnose, galactose, mannose, inositol, oxalate, citrate, acetate, propionate, lactic acid, tartrate and succinic acid, but with different efficiency.

The activity of the key enzymes α -ketoglutarate carboxylase and isocitrate lyase has been examined in these species (Baran et al. 2003). Enzymatic activity of α ketoglutarate carboxylase and isocitrate lyase in *Thiocapsa* and *Lamprocystis* culture cells may suggest the functioning of an incomplete tricarboxylic acid cycle and the absence of a glyoxylic pathway in their cells. The catalase activity of all the investigated bacteria appeared low, which testifies to their sensitivity to molecular oxygen of air (catalase is an enzyme of the antioxidant defence system in cells). It was shown that isolated purple sulphur bacteria are capable of actively oxidizing hydrogen sulphide (23-32 μ M/h). The rate of oxidizing H₂S by purple bacteria in laboratory conditions is similar for both species

(Figure 5). These data allow the calculation of the rate of oxidation and comparison with the chemical process. Annually, *T. roseopersicina* is able to oxidise 23.3 μ M H₂S, and *L. roseopersicina* 31.95 μ M H₂S, whereas without bacteria only 1.84 μ M H₂S is oxidised. The biological process is 12-17 time more effective (Kit et al. 2004). Oxidizing H₂S by another consortium, *Pelodictyon luteolum* and *Chlorobium limicola*, isolated from Yavoriv's reservoir, is less effective – only three times faster than in chemical conversion (Baran et al. 2003).

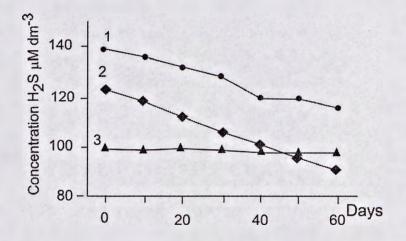


Figure 5. Rate of oxidation of H_2S in the presence of phototrophic purple bacteria in laboratory conditions. 1 - T. roseopersicina; 2 - L. roseopersicina; 3 -control. (Kit et al. 2004).

Sulphur bacteria are present not only in the reservoirs. The whole region around the opencast sulphur mines near Yavoriv is contaminated by sulphur. Gudz et al. (2002) analysed the content of sulphate-reducing bacteria in the mud of streams flowing across this area. The number of these bacteria in streams flowing into small dam reservoirs is lower than in streams without reservoirs. The number of sulphate-reducing bacteria varied greatly with the season, which means that they are dependent on temperature. In winter, the number of these bacteria amounts to 50-1000 cells per 1 g of wet mass sediment, whereas in summer, the number is ten times greater

Phytoplankton

The conditions in Piaseczno reservoir are favourable for not numerous scarce algae species. The photosynthetically active light range limits the occurrence of phytoplankton to 10–12 m layer (Figure 6). In low numbers, algae were noted up to a depth of 15 m. No algae were found at depths of 20 and 22 m. Exceptionally at the end of April, there were numerous diatoms of the species *Navicula rhynchocephala* present in the monimolimnion. These diatoms are probably able to live in darkness and in an anoxic hypolimnion and monimolimnion in the presence of sulphide, (Wilk-Woźniak & Żurek 2006).

The specific chemical properties of the environment limit phytoplankton development, thus effecting a simultaneous reduction in the diversity and abundance of species. Phytoplankton analyses indicated a poverty of species structure and quantity. During mid summer, the chrysophyte *Dinobryon divergens*, dinoflagellates *Peridinium*, *Ceratium* and the cyanobacteria *Anabaena* (early summer) develop intensively. Coccal green algae, diatoms (*Cyclotella radiosa*) and euglenophytes (*Trachelomonas volvocina*) were among the other numerous species noted. The chrysophyte *Dinobryon divergens* developed very abundantly (2.4 x 10^6 cells L⁻¹) in the epilimnion in August. The cyanoprokaryote *Anabaena minderi* occurred fairly numerously in the near surface layer (2.5-5 m at 19.2- 12° C) in June.

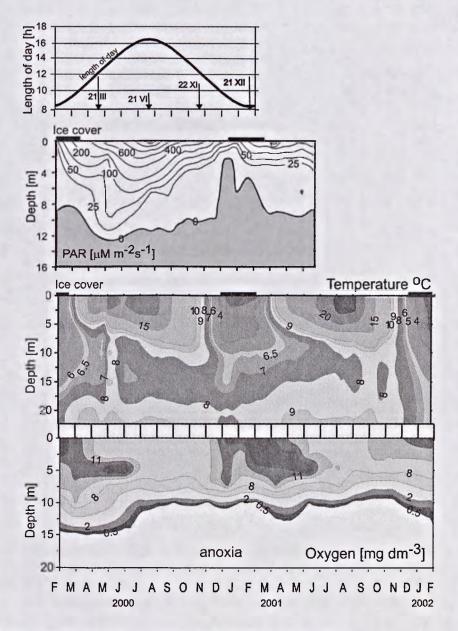


Figure 6. Luminous and oxygenic conditions in the reservoir

Zooplankton

In the Piaseczno reservoir were found 20 species of rotifers, six species of Cladocera, and eight species of Copepoda. A single Ostracod and *Chaoborus flavicans* were also noted in the samples.

After detailed analysis of the community structure, the period of appearance, the place of appearance, the position in the reservoir and the coexisting species, many detailed realationships were discovered.

In the winter, the upper 10 m layer of very cold water dissolves a great amount of oxygen. Later, when the thermocline is formed, these well-oxygenated water masses slip below the thermocline where they remain until the end of July when the warm epilimnion becomes thicker and the thermocline becomes fuzzier (Figure 6). Then the O_2 concentration diminishes and this wedge vanishes. In consecutive vertical profiles, the shift of depth where the highest density of *Brachionus angularis* is found is visible. When this population dislocates to a deeper level, it remains in cold, well-oxygenated water. When this wedge vanishes, the population of *B. angularis* also vanishes. *Chydorus sphaericus* has a similar preference.

The high content of solutes is a selective factor for some planktonic animals. Generally, a solute concentration of c. 2000 mg is tolerated by most freshwater species. On the other hand, it is also high enough for species characteristic of brackish water. Here an example is the rotifer *Hexarthra fennica*, a species known to survive in highly mineralised soda lakes or brackish water. It chooses to occupy the warm subsurface layer – it avoids competition with other species which prefer the deeper zones. In winter and early spring, the entire mixolimnion is occupied by cold stenothermic species like *Polyarthra dolichoptera* and *P. bicerca*. The temperature of the hypolimnion, 7–9 °C, provides a refuge for cold water species, which can survive the summer without diapause or

the production of resting eggs. The number of these cold stenothermic species in summer is low due to competition with summer species that can tolerate these temperatures.

In summer, zooplankton relationships become complicated: the epilimnion is warm but poor in algae, and the resulting good visibility is beneficial to fish. Below the thermocline the temperature decreases by 10 °C, but it is still enough light so algae are more numerous, but due to their size or the possession of spines they are less suitable for consumption. Fishes avoid this layer but there are many invertebrate predators: *Asplanchna sieboldi, Thermocyclops crassus, Acanthocyclops robustus, Diacyclops languidoides* and *Cyclops vicinus*. These predators are also at risk – in the hypolimnion they are the prey of *C. flavicans* and fishes as well. Despite this risk for zooplankton, there is a lot of bacteria for consumption. Exploitation of this food resource is hard due to the lack of oxygen and the presence of H_2S/HS^- . Survival is possible due to the specific adaptations that plankton have developed during their long evolution. Furthermore, plankton use all possible strategies to survive.

• *Succession and seasonality.* In spring the environment is dominated by rotifers. Later, copepods develop, then when the copepod population declines, cladocerans achieve success by diminishing the chance of predator encounters.

• *Choice of position in space*. Usually, the epilimnion is monopolised by rotifers, whereas the hypolimnion has a more diverse assemblage of rotifers, cladocerans and copepods. Rotifers are too small to be convenient food for fishes (excluding fry, but they prefer the littoral zone). Niches are chosen by slowmoving, soft-bodied species that are devoid of other defence possibilities, for example *Synchaeta*, nauplii, cladocerans.

• Defence by an armoured body. Rotifers of the genera Keratella (cochlearis, hiemalis, quadrata) have this type of defence. It is effective against grasping predators like copepods, but not effective against swallowing predators like As-

planchana. When predation pressure is too strong, as in the hypolimnion, softbodied species are, in practice, absent.

• Defence by jumping. This technique is used by Polyarthra species, Hexarthra or copepods. Being able to quickly spring out of the attack range is effective.

• Defence by apparent size. The long spines of *Filinia longiseta* and *Kelliqottia longispina* are and effective passive defence against invertebrate predators.

Defence by jink. This is in the sense of diel vertical migration (DVM). Some species migrate across the thermocline, others, like *Keratella*, have two temporary subpopulations divided by the thermocline. Each has an independent DVM. Some species prefer a constant position. Both a typical and reverse DVM (like *S. tremula*) is realised. More detail can be found elsewhere (Żurek 2006b).

Chaoborus flavicans.

The hydroacoustical method was used in the examination of the Piaseczno reservoir. The echo sounder showed weak sound scattering particles with the target strengths peaking at -59 dB in spring and -55 dB in autumn at the depth corresponding roughly to the lowest limit of oxygen concentration. Later these objects were identified as *Chaoborus flavicans*. During spring, these targets occupied depths of between 13 and 15 m (mean 14.2 ± 0.9) during the day, and between 10 and 12 m (mean 11.3 ± 0.7) at night (Figure 7). In autumn the layer moved up, with the majority of the targets being found at depths of 9–11 m (mean 10.1 ± 0.6) during the day, and 6–7 m (mean 6.5 ± 0.3) at night. The density of *Ch. flavicans* was estimated on 1322 and 2560 ind. ha⁻¹ = 0.13 – 0.25 ind. L⁻¹. Planktonic sampling confirmed the ability of these species to penetrate H₂S zone.

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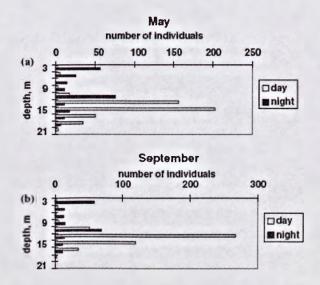


Figure 7. Vertical distribution of non-fish targets – *C. flavicans*. (Godlewska & Jelonek 2006)

Benthos

The benthic fauna consists of 42 macroinvertebrate taxa. The meiobenthos and Protozoa were not investigated. Oligochaeta (Tubificidae) and Chironomidae predominate. Exclusively ubiquitous species were found, except for some chironomid taxa recorded for the first time in Poland. The bottom sediments contain 2.7- 8.8 % of organic matter. The density of benthic organisms does not depend on the organic matter content of the bottom sediments. Fifteen taxa of Chironomidae and 13 taxa of Oligochaeta are represented (Dumnicka & Galas 2006). Among the Chironomidae, only the larvae of the genus *Procladius* dominate in all the examined transects. The accompanying Chironomus sp. and Tanytarsini juv. were also numerous. *Chaoborus flavicans* was abundant at the 5 m

depth station and it was found in the greatest proportion at 10 m (54.5% of the total benthic community). In the planktonic samples, these larvae were noted in the pelagial zone at a depth of 10-15 m, and single individuals were found near the bottom at 20 m.

Among the Oligochaeta, juvenile forms from the family Tubificidae predominated and were present up to a depth of 10 m. These included *Tubifex tubifex, Limnodrilus hoffmeisteri, L. claparedeanus* and *L. profundicola.* The majority of taxa found in Lake Piaseczno are detritivorous (Tubificidae, *Chironomus* sp., Tanytarsini), but predators (*Procladius* sp.) and algivorous species (*Nais* sp. and *Lymnaea* sp.) occurred only in small numbers.

Fishes

All fishes were introduced by the 'bucket method' by anglers. Professional investigations carried out 21-22 years after inundation recorded ten fish species in the Piaseczno: *Abramis bjoerkna* (L.), *Rutilus rutilus* (L.), *Scardinius erythrophthalmus* (L.), *Alburnus alburnus* (L.), *Perca fluviatilis* L, *Leuciscus cephalus* (L.) and *Gymnocephalus cernuus* (L.) in the littoral zone; *Carassius auratus gibelio* (L.) and *Leuciscus leuciscus* (L.) in the pelagial zone; and *Esox lucius* (L.) occurred in both zones. In this set of species lack the common elsewhere *Abramis brama*. Only the first five species have a relatively important position in the fish community of the Piaseczno. The above species list is half that of the Vistula River. Evidently, this fish community originated from the pool of species occurring in the neighbouring reach of the Vistula and its valley, i.e. in its main channel, dead arms, tributaries, fish ponds, etc., located in the close vicinity of the Piaseczno.

For the estimation parameters of the fish population, few techniques were used (Godlewska & Jelonek 2006; Amirowicz, unpubl). Sampling was done by a pe-

lagic non-selective set of gill nets of nine different mesh sizes (11–60 mm knot to knot). The nets (2 m deep) were set for 12 h (day or night) within two depth zones: 0-2 m and 4–6 m. Catch per unit effort (CPUE) was calculated as the number of fish per 1000 m² net area per 12 h.

Distribution. The hydroacoustical method was used in the examination of the Piaseczno reservoir. This method was supplemented by classic net catches. The group of strongly scattered sound targets (fishes) was recorded randomly above the anoxic zone, i.e. in the epilimnion and upper hypolimnion. Complementary net fishing (especially in the dead zone at 0 - 2 m) showed a preference of fishes for thin (2 - 3 m), warm water above the thermocline in spring and summer. Later in the autumn, when the the warm epilimnetic layer was greater and the thermocline was deeper, fishes preferred a depth of 4 - 6 m (Figure 8).

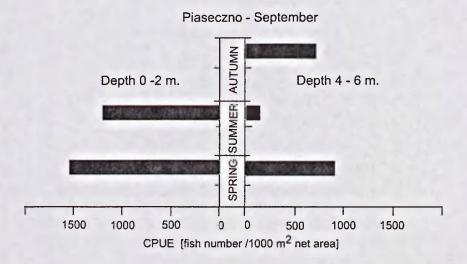
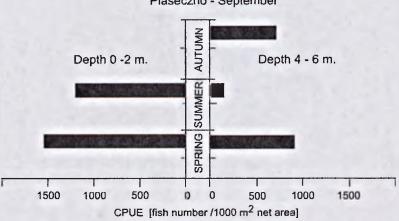


Figure 8. Fish distribution in layers 0–2 m and 4–6 m from gill nets in spring, summer and autumn (Godlewska & Jelonek 2006). CPUE – catch per unit effort.

Apart from the vertical distribution of fishes, seasonal changes in horizontal distribution were observed. In spring and early summer in the pelagic zone, fish densities were 280 ha⁻¹ and 530 ha⁻¹ in autumn. These hydroacoustical observations were confirmed by Amirowicz (unpubl), who put gill nets in the surface layer (0– 2.5 m) in both the littoral and pelagic zones; 116 fish were caught in May but only 22 in September. In both cases, over 80% of all fish were caught in the littoral zone. This clearly indicates an autumnal migration of fishes from the littoral zone, which is rich in food, into the pelagial zone, which is considerably impoverished in food.

Abundance. Hydroacoustical surveys in the Piaseczno reservoir revealed very scarce fish populations in pelagic waters with double the abundance in autumn (530 fish ha⁻¹) compared with spring (280 fish ha⁻¹). This is a lower value than found in the mesotrophic Dobczyce reservoir (Figure 9).



Piaseczno - September

Figure 9. Comparison of fish abundance in the Piaseczno and Dobczyce dam reservoirs. Densities and biomass are expressed in relation to the maximum value of CPUE, which was assumed as 100%. Acc. to Amirowicz (unpubl.).

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The life history of roach. The achievement of a large size and older age in this reservoir is not easy for fishes. As mentioned above, only five species are important (roach, white bream, rudd, bleak and perch), and the remaining species are rare. Undoubtedly, fish stocking was random and accidental. Some facts or relationships in this community can be easily explained, but others remain without explanation. The low numbers of dace and chub in the reservoir is easy to explain: the lake ecosystem is probably an inappropriate environment for riverine species. The rarity of goldfish and ruffe is difficult to explain. The dominant position of the roach population confirms the supposition of relatively good adaptation of this species to the habitats of the Piaseczno reservoir. Roach have about 1.5-2 times greater relative abundances in the pelagial zone than in the littoral zone. Perch, inversely, are more numerous in the littoral than in the pelagial zone. This difference is statistically significant (P<0.01). For all fishes generally, the littoral zone was more friendly than the pelagic zone in units of CPUE.

Roach was used to test Lee's phenomenon. The back-calculations of standard length from scales and appropriate statistical methods showed three phases in the life of roach.

During the first stage from hatching until the end of the third year of life, growth is very good, i.e. very fast. In the fourth year, a shift in growth occurs in the Piaseczno. During the second stage, lasting to the end of the seventh growing season, the growth rate of roach can be classified only as average or average/slow. In the last two age classes, again a considerable acceleration in growth is visible.

Amirowicz tried to explain this fast growth stage. Alimentary conditions after switching to feed on molluscs cannot be accepted. There are no clams and snails except *Lymnea*. Then he tried to analyse fecundity. Fecundity was on average equal to 1.1-1.8 of the reference from the Mazurian Lakeland. This

seems to be the correct explanation for the slowed growth rate after maturation (i.e. as in the second stage of roach growth), as there is an effect of a shift in resource allocation forced by the trophic conditions. The life history of roach in this specific reservoir is complex. In the first phase, the most important aspect may be the investment in individual growth for, e.g., reduction in predation risk, which leads to maximizing future fecundity. The change to this strategy is probably caused by the shift in feeding conditions. For adult roach in the Piaseczno, the most profitable strategy may be investment in current fecundity, even if it may lead to growth retardation. The high position of roach in the fish community confirms the effectiveness of this strategy.

Birds

Birds were investigated by Gwiazda (unpubl). Special attention was devoted to investigation water bird communities (structure and density) and determining the foraging techniques of water birds in this habitat. At the time of the observations, the water body occupied c. 30% of an opencast area, where the total area of helophyte vegetation in the littoral zone and around the water body was more than 20 ha. Most of the shoreline was steep and covered by aquatic macrophytes (*Potamogeton, Phragmites, Typha* spp.), flooded willows and shore vegetation of shrubs and trees. The remaining area of opencast, i.e. between the water table and the plateau, had an area of c. 100 ha and was covered by reeds, grass, shrubs and self-seeding trees.

Twenty-six species of water and marsh birds (including passerines) associated with water habitats were found. Nine species were recorded only once or twice. The densities of birds varied in widely, from 4.2 to 26.9 individuals per hectare (median 13.0).

As Gwiazda (unpubl) reports, the dominant species were great crested grebe,

mallard, coot *Fulica atra*, black-headed gull *Larus ridibundus* and herring/ yellow-legged gull *Larus argentaus/cachinnans*. Eight ichthyophagous species were the most abundant. Entomophagous and phytophagous birds (6 species) and waders (3 species) were not frequent or abundant. Relative abundance (total number in all visits/number of visits) was greatest for great crested grebe and mallard (both species comprised more than 17% of the water bird community). The number of great crested grebes, *Podiceps cristatus*, were almost constant.

Phytophagous species such as mallard and coot, occurred mainly in the macrophyte vegetation. Benthophagous species (pochard *Aythya ferina* and tufted duck *Aythya fuligula*) were very scarce (except for the flock of pochards). Yellow-legged gulls occurred mainly in the central part of the lake. The great crested grebes were randomly spaced: they did not prefer any particular parts of the reservoir.

Piaseczno offers only a deep, open water habitat with a relatively small littoral zone and a very poor food base, but with a large area of vegetation around the shore. This could explain why a great number of the species recorded at Piaseczno were seen irregularly and rarely. The neighbouring large Vistula River is very important as a passage route for water birds during migration (Bocheński 1991). Only some migrating birds visited Piaseczno.

The number of breeding species was also small in comparison to ponds (4 - 57 species) (Dobrowolski, 1995) and dam reservoirs (33-41 species (without passerines), (Stawarczyk & Karnaś 1992; Gwiazda 2000). Other water bodies near the Vistula River also have a greater number of breeding species – 7 to 30, (Wiehle et al. 2002). This can be attributed to the narrow littoral zone, the lack of very shallow water and the muddy bottom, which offer poor foraging and breeding conditions for water birds. This can explain both the low densities and low numbers of water bird species on this reservoir. However, it

does not explain the next question: why are the densities of great crested grebe often higher than elsewhere?

Usually, the density of great crested grebe on ponds are 0.4-2.4 pairs/10 ha (Gwiazda 1996), and on small gravel pits, dam reservoirs and in many large lakes in Europe 0.5-3.0 pairs/10 ha have been recorded (Hageneijer & Blair 1997). This relatively high density of pairs (1.2 pairs/10 ha) cannot be explained by a high density of fish prey for this species, because fish density and biomass is very low at c. 30 /ha. Hydroacoustical investigations have revealed very scarce fish populations in the pelagic waters with double the abundance in autumn (530 fish ha^{-1}) compared with spring (280 fish ha^{-1}). Small and very small fish (below 10 cm length) dominated (Godlewska & Jelonek 2006). The explanation must lie elsewhere. It is known that the detection volume of diving birds is a hemisphere with a radius given by the water transparency (Eriksson 1985). The availability of fish, depending on the survey volume in which fish can be detected, is more than four times greater in the oligotrophic Piaseczno reservoir than in the eutrophic Dobczyce reservoir (on the River Raba, Poland) (Gwiazda, unpubl). To the crested grebe, this type of reservoir is propitious. Fishes are located only in the 10 m upper layer above the anoxic hypolimnion. The described mechanism cannot be used for 'surface plungers' such as gulls or terns, which search for fish from above. The common tern and gulls did not breed at Piaseczno but visited for foraging or resting. The remaining dominant species are common in other water bodies and reservoirs in Central Europe, including Poland.

Mines as source of waste

During the active exploitation of Polish mines, $84 \times 10^6 \text{ m}^3$ surface water and $1.4 \times 10^6 \text{ m}^3$ of ground water was used. The discharge of waste was $76 \times 10^6 \text{ m}^3$. The annual load of discharged wastes (in different years of exploitation)

contained 31,000– 222,000 tons of sulphate, 62,000 – 372,000 chlorides, 61– 756 tons of fluoride and 556 – 29,438 tons of suspensions. The annual emission of dust and gases oscillated between 25,000 to 2,896 tons. Solid wastes were 2.5 x 10⁶ tons annually. With time, these parameters improved. Sulphur mining in Ukraine also had problems with draining water discharge. From the Yavoriv opencast mine the daily discharge amounted to 13,000 m³. Annually, this was 48 x 10⁶ m³ of water. The mean solute concentration was 3.6 g L⁻¹ and of this 1.6 g was SO₄. Besides this, water had up to 50 mg L⁻¹ of H₂S. After recalculation, these data show that the receiving stream was loaded with 173,000 tons of salts (and of this 120,000 tons was CaSO₄) and 240 tons of hydrogen sulfide (Gaydin 2000).

Comparison with other mining lakes and circumneutrals of glacial origin

Almost all post-mining meromictic lakes, both acidic and neutral, have a common feature: the same trophic state – oligotrophy, and sometimes mesotrophy. These reservoirs have low productivity and good transparency. The littoral zone is usually narrow or doesn't exist in the bluff banks. Food resources can support only small fish and bird populations. What processes lead to this state? The barrier to primary production, which diversifies the strophic state, is usually phosphorus or nitrogen, and rarely Fe or other elements. Let's compare acid and neutral meromictic reservoirs. The water reaction in the vertical profile is reversed in these types of reservoir: In acid reservoirs the epilimnion is more acid (ca. pH=3) than the hypo- and monimolimnion (5.5–6.3). In post-sulphuric reservoirs, inversely the pH of the epilimnion is *c*. 8, whereas the hypo- and monimolimnions are neutral or weakly acid.

Both kinds of reservoirs have high concentrations of P in the vertical profile from surface to bottom. Both kinds of reservoirs have a high concentration of sulphur compounds, but in acid reservoirs, iron is the dominating cation, whereas in post-sulphuric reservoirs it is calcium.

The next common feature is the very low concentration of nitrate in the photic zone. Part of this nitrogen form is exploited by phytoplankton, but most is trapped in the hypo- or monimolimnion as NH₃/NH₄. In Piaseczno, cyanobacteria such as *Anabaena minderi* are able to assimilate free nitrogen. After decay and transformation, each absorbed H⁺ ion in the reaction NH₃ + H⁺=NH₄⁺ brings an increase in alkalinity. It is one of the few possible pathways to increasing pH, especially in the aphotic zone. This process is possible only in lakes with pH > 4 to 5, due to absence of cyaonbacteria below this threshold, Steinberg et all. (1998).

Other reasons for decreasing NO₃ are important. The nitrate serves as a terminal electron acceptor for anaerobic respiration. This aphotic zone has high concentrations of CO₂ at 17–270 mg L⁻¹. Elevated pCO₂ enhances nitrate reduction. Related reactions follow:

 $5H_2S + 2HNO_3 \rightarrow 5S^\circ + N_2 + 6H_2O$

or

 $5H_2S + 8HNO_3 \rightarrow 5H_2SO_4 + 4N_2 + 4H_2O$

Sulphuric acid makes gypsum in the reaction H_2SO_4 +CaCO₃+H₂O=CaSO₄·2H₂O +CO₂.

The reaction of H_2SO_4 neutralization is effective in post sulphur mines rich in calcium. Other acid or acidic lakes such as lignite pits are poor in Ca and Mg. There, the process of neutralization occurs slowly over several dozen years.

The competition for nitrogen is won by bacteria, for the algae does not leave much N. This process seems to control the nitrogen (nitrate) level in the

reservoir with all consequences for a trophic state both in circumneutral and acidic lakes. The described mechanism explains the nitrogen limitation of the whole food chain from the bottom up.

Intensive oxidizing H₂S in post sulphur mines, causes the precipitation of CaSO₄ and the co-precipitation of phosphates succoured with sulphides (Danen-Louwerse 1995; Noda et al. 2002). In effect, PO₄ concentrations in the hypolimnion and monimolimnion are half that in the epilimnion. In acidic lakes Fe is important in PO₄ precipitation as FePO₄. This process seems to confirm the positive and significant correlation (r=0.98), between Fe and PO₄ in the sediments of acid lakes. In reservoirs with pH > 5.17 and in a state of Fe oversaturation, precipitation of Fe(OH)₃ occurs. These precipitated Fe and Al hydroxides act as substrates for phosphate sorption – this is the other path of P circulation.

These limitations of a 'bottom up' type cause the transfer of matter to occur mainly through the bacterial loop. Investigations of phytoplankton confirm the presence of numerous flagellates, which are bacteria consumers. Also, the zooplankton of the hypolimnion was composed of up to 60 - 90% rotifers, which feed on bacteria. These bacteria are significant primary producers at the base of the meromictic lake food chain both in acid and alkaline reservoirs. Of course, in acid reservoirs and in spite of their origin, the low pH eliminates non tolerant species.

Najbar (1998) analyzed richness of zooplanktonic communities in acid, transitional and neutral reactions of post lignite mining lakes. In a group of eleven acid reservoirs (pH <4) he found 21 species of animals. There were only two species of copepod in one of the eleven acid reservoirs; two species of Cladocera in two reservoirs, and eight species of rotifers. The accompanying species found in the different reservoirs included Rhizopoda, Ciliata and Flagellata.

Transitional reservoirs (pH 4.1-5.6) had the richest planktonic fauna with 72 species. Rotifers were especially numerous with 35 species, and there were seven species of copepod and three species of cladocerans. The remaining planktonic animals were not numerous: only one species of Gastrotricha and two species of Ostracoda were found. In the neutral reservoirs (pH 6.0-7.9) 61 species of rotifers, 11 copepods and 11 cladocerans were found.

A similar situation was observed during the peak of anthropogenic acidification by acid rain (1978-1996) of the lakes in the West and High Tatra Mountains. The reference zooplankton assemblages of the Tatra lakes are known from historical studies since the middle of the 19th century. In strongly acidified lakes (criteria: pH <5.2, alkalinity <0 μ eq L⁻¹, calcium <50 μ eq L⁻¹) original zooplankton disappeared (*Cyclops abyssorum, D. longispina, Mixodiaptomus tatricus*) except for acid tolerant *Chydorus sphaericus* that become dominant (Hofická et al. 2006). In some Polish lakes of the Tatra Mountains (with pH 4.6-4.9) it was the only crustacean. Hofická et al. 2006 recognized that acidification-induced oligotrophisation was a crucial mechanism in the disappearance of the species. When pH is one unit higher i.e. 5.0 to 6.1, then the environmental conditions are acceptable for most algal and animal species.

Liquidation - prognosis, approaches and techniques used

The two approaches to the liquidation of mine pits are financial and ecological. When a financial threshold is the limiting factor, the investor decides to flood an open pit "as it is". This liquidation model was used in Yavoriv mine. As it proved to be successful, this technique will be applied to Podorozhne mine. At present, Lake Yavoriv is of meromictic type, with good transparency, of mesotrophic state, and oxygenated epi-

and hypolimnion. The model applied to Machów and Rozdol mines was the opposite to the above-mentioned. There sulphur outcrops were isolated by 15 - 20 m layer of clay and silt. Such a method is expensive, long-lasting but usually results in better water quality. The first mine was flooded by riverine water (from the River Vistula), whereas Rozdol mine was flooded by surface and underground waters. Flooding by riverine water gave better results – lower hardness and lower concentrations of typical anions, especially sulphate.

The new reservoir of Machów is dimictic, stratified and of mesotrophic state. The new reservoirs of Rozdol filled with underground water have very hard water with SO₄ concentrations 1600–2000 mg L⁻¹ and good transparency. A shallower reservoir is polymictic (Srednie), a deeper (Glubokoe) – dimictic.

After 28 years from the termination of exploitation in the Piaseczno, the formation of the bottom and slopes of the reservoir commenced (Figure 3). 2009 is the first year of the 5-6 annual period of full flooding. Adopted strategy of liquidation is intermediate.

Engineers have employed a five-meter silt isolation of outcrops only above the water table of the partially filled reservoir and left the reservoir to be filled with rains and underground water. Such a technology will bring no changes. The mixing type should remain meromictic, of the same trophic state (oligo- to mesotrophy, with high concentration of sulphate and good transparency. Engineer's and hydrobiologist's opinions are different as regards further evolution of this reservoir. The key differences concerns interpretation of modelling procedures and results. The basis for water quality prognosis was the detailed water balance (Table 6) and modelling of the flooding process.

| State | Ordi- nate | Constituent of balance | | | | | | | |
|------------------------------|---------------|------------------------|----------------|-----|-----------------------|----------------|----------------|------------------------------------|-----|
| | m asl. | Q _P | Q _E | Qs | Q ₁ | Q ₂ | Q ₃ | Q ₄ + Q ₅ | Q7 |
| Initial state | 122.4 | 768 | 922 | 156 | 3601 | 3098 | 4202 | 1808 | 538 |
| Prognos- ticated state | 146.0 | 2496 | 2995 | 53 | 1289 | 3811 | 0 | 154 | 269 |

Table 6. Basic sources of the hydrological balance for the Piaseczno reservoir. Efficiencies of inflows/outflows $[m^3 d^{-1}]$ (Kirejczyk et al. 2007).

Where:

- Q_P direct precipitation on reservoir surface
- Q_E evaporation from reservoir surface
- Q_S surface run-off from reservoir basin
- Q_1 quaternary underground inflow through dump
- Q_2 inflow through remaining quaternary alluvia
- Q_3 inflow through quaternary alluvia from Vistula River
- Q_4 inflow of tertiary water through 'hydrogeological window' (on W and N-W from pit), flux through inner dump
- Q_5 inflow of tertiary water from 'hydrogeological window' (on W and N-W from pit), flux bypassed inner dumping ground

 Q_7 – inflow of tertiary water from remaining area of infiltration, mainly on E from pit.

During the reclamation project, Kirejczyk et al. (2007) tried to calculate the mean concentrations of the trace ions chloride and sulphate in the Piaseczno reservoir at the final water level of 146.0 m asl. For the actual water level (122.4 m asl) model (MODFLOW), the anticipated chloride concentration was 153 mg L^{-1} , i.e. similar to the concentration in the surface layer. For this reason, the authors consider that the model result is correct. Hydrobiologists cannot agree about treating the meromictic lake as perfectly polymictic. The model used by engineers did not take into account the correct mixing type. However, the inflow of tertiary water will diminish from 2,348 m³d⁻¹ at present to 423 $m^3 d^{-1}$ in the future, and the reservoir will remain meromictic. Frankiewicz & Pucek (2006) have a similar opinion. Despite this, the new equilibrium state will be established. Hitherto examples and strategies of liquidation make it possible to indicate the best technology. When underground water is planned for flooding the opencast, isolation of outcrops is useless. Chemical mechanism of meromictic reservoir vouches good transparency and trophic state of the surface water layer. When river water is planned for filling – outcrops should be isolated.

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