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Changes of groundwater chemistry caused by the flooding of iron mines (Czestochowa Region, Southern Poland)

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Abstract

Underground mining always causes disturbances of the hydrogeological environment, primarily due to the dewatering of mine workings. The flooding of abandoned mines contributes to the rebound of the cone of depression developed previously, but it also leads to significant pollution of groundwater in the mined areas. The Middle Jurassic aquifer in the Czestochowa region of the flooded iron mines has been investigated with respect to patterns of water movement and groundwater chemistry. Basing on eight years of studies including field measurements, data collection and physicochemical analyses of groundwaters, two models has been developed: a hydrological model of water flow and a hydrochemical speciation model. Additionally, in order to validate the results, stable isotopes of hydrogen and oxygen, together with tritium and radiocarbon, have been analysed. Four distinct hydrochemical zones has been identified within this aquifer based on the results of these studies: Zones I and II — where the groundwater is influenced by iron mining, and Zones III and IV — where the groundwater in the Middle Jurassic aquifer is uncontaminated. The results indicate that the changes in groundwater chemistry within the flooded iron mines area are significant. Maximum SO_4^{2-} contents reach 1103.0 mg l^{-1} and are 6 times higher than the acceptable levels for human consumption of water (Polish Drinking–Water Limits), Mn^{2+} contents reach 6.61 mg l^{-1} and are 70 times higher, and Fe_{tot} reach 271.4 mg l^{-1} and are 500 times higher. Water flow modelling and hydrogeochemical interpretations suggest that waters in the zone III, in spite of their occurrence within the area of the cone of depression caused by the iron mining, are not influenced by the polluted mine waters. This is corroborated by the isotopic investigations. The age of waters from this zone has been determined as Early Holocene, which strongly suggests that these waters had recharged before the dewatering began.

The results of the hydrochemical studies suggest that fifteen years after the flooding, waters stored in the mine workings may be defined as quasi-stagnant. Middle Jurassic aquifer water supplies located in Czestochowa are not polluted by mine waters today, but the predicted contamination of waters will occur in the first supplies at the end of the 21st century. However, it may last for 300–500 years. The general conclusion is that if the formation of the polluted acid and neutral waters in such mined sedimentary ores as in the Czestochowa region is not prevented, the residual pollution of groundwaters in the flooded mines may persist for several centuries.

Keywords: Groundwater; Acid mine drainage; Hydrochemistry; Environmental isotopes; Modelling

1. Introduction

The hydrogeological environment is always altered by mining activities, mainly due to the drainage of the aquifer, which results in the formation of the cone of depression (Rubio and Lorca, 1993) and the reduction of groundwater resources. The lowering of the groundwater table changes groundwater recharge and discharge (Pigati and Lopez, 1999) and causes

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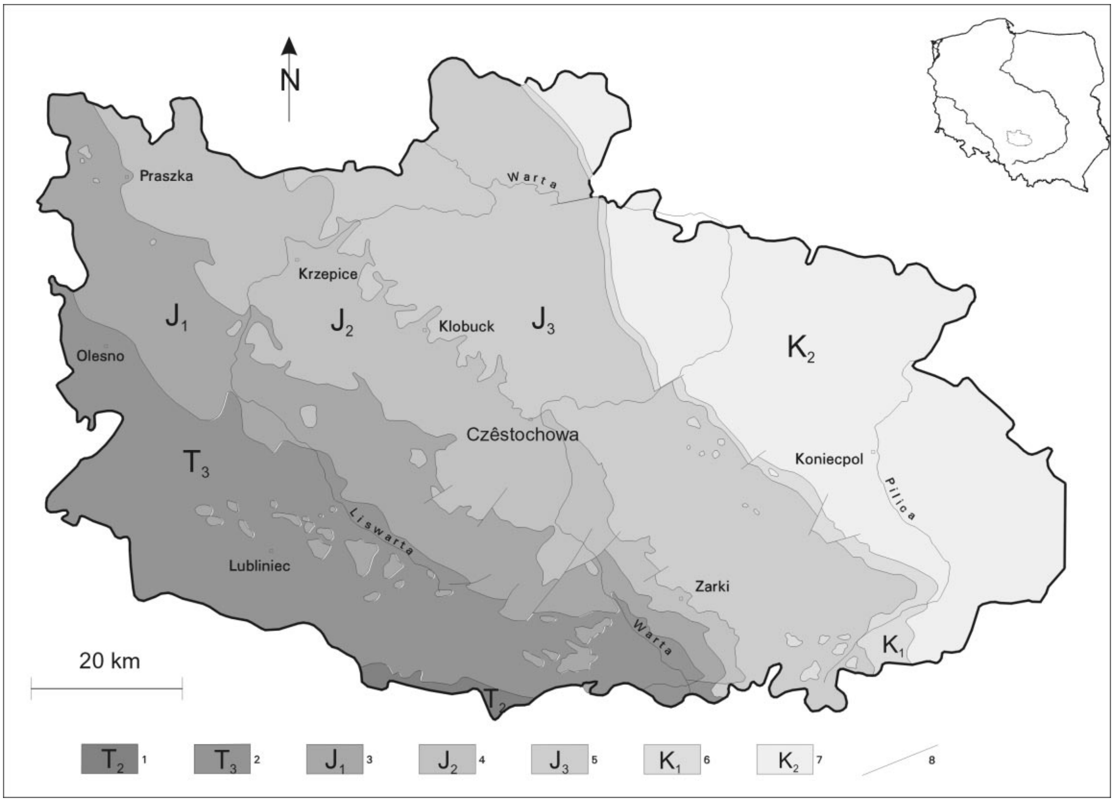


Fig. 1. Schematic geological map of the Czestochowa region without the Cainozoic sediments (after Wielgomas red., 1981). The location of the Czestochowa region on the map of Poland is in the upper right corner. 1 — Middle Triassic; 2 — Upper Triassic; 3 — Lower Jurassic; 5 — Middle Jurassic; 6 — Upper Jurassic; 7 — Lower Cretaceous; 8 — Upper Cretaceous; and 9 — faults.

catchment modifications (Dudgeon, 1999). Acid mine drainage generation (AMD) is another one of the most important problems connected with mining activities (Gray, 1997; Geldnehuis and Bell, 1997; Sherwood and Younger, 1997). Barnes and Clarke (1964) described the generation of AMD for the first time, and characterised pyrite or marcasite as the initial sources of the mine quality decay. The flooding of the mines causes the rebound of the cone of depression but it also leads to significant pollution of groundwater in the mined areas (Cairney and Frost, 1975; Foos, 1997; Grmela and Rapantova, 1997; Rosner, 1998). Longevity of mine water quality deterioration due to the abandoning and flooding of mines in the UK has been reported by Banks et al. (1996), Chen et al. (1997) and Woods et al. (1999). The problem of changes in groundwater chemistry caused by the iron mining in France was described by Ammou et al. (1982) and Ramon and Ricour (1993). Mayo et al. (1992) demonstrated the significance of the use of solute and isotopic chemistry to identify flow patterns and factors which limit acid mine drainage.

Until early in the 1980s, there were underground iron mines operating in the Czestochowa region. The oldest documented mining took place in the late 14th century, while the underground mining began in the late 18th century (Adamski, 1994). Water was pumped from the underground iron mines for over 50 years, and the groundwater table was lowered below the mine levels, causing the Middle Jurassic aquifer to be dewatered. The regional cone of depression in the Middle Jurassic aquifer caused by water pumping from the iron mines was about 20 km wide, 50 km long and its depth reached 130 m (Razowska et al., 1997). After 1970 the government decided to close

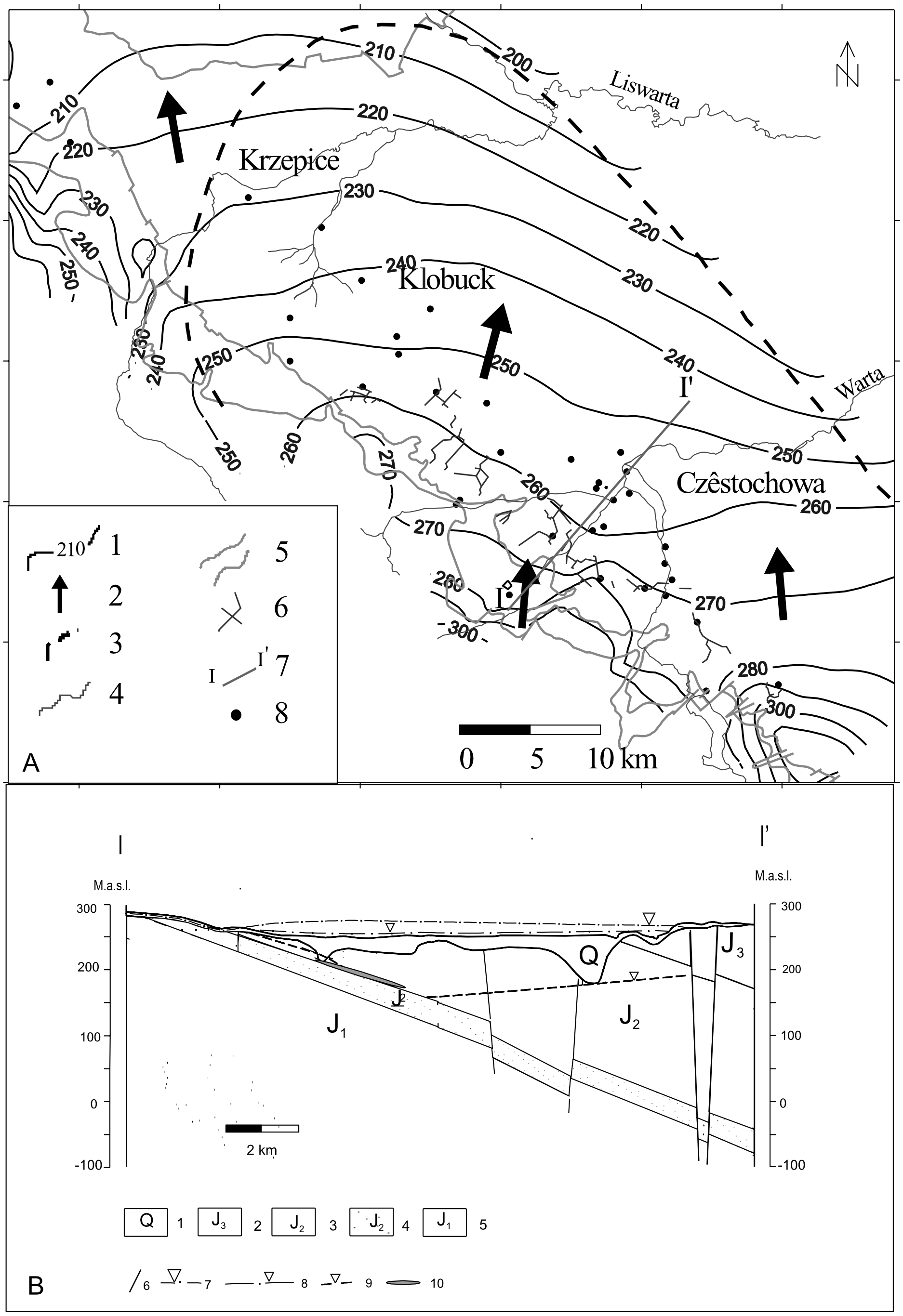


Fig. 2. Hydrogeological map (A) and cross-section (B) of the Koscieliska aquifer in the Czestochowa region. A: 1 — water table countours in metres above sea level (1996); 2 — direction of groundwater flow (1996); 3 — maximum extent of the cone of depression caused by the iron mining (1967); 4 — rivers; 5 — outcrops of the Koscieliska strata; 6 — water galleries of iron mines; 7 — line of the hydrogeological cross-section; and 8 — wells and mine shafts. B: 1 — Quaternary deposits; 2 — Upper Jurassic limestones; 3 — Middle Jurassic iron-bearing clays; 4 — Middle Jurassic sands and sandstones (Koscieliska strata); 5 — Lower Jurassic siltstones and mudstones; 6 — faults; 7 — groundwater table (natural level); 8 — groundwater table (1996); 9 — groundwater table during dewatering (1967); 10 — wells; and 11 — water galleries of the iron mines.

the iron mines in Poland due to the economic factors. Dewatering ceased, all the mines were closed and allowed to flood. The groundwater table started to rise and now the rebound in the former cone of depression is almost complete as is demonstrated by flowing wells near Czestochowa. The hydrogeological environment of the Middle Jurassic aquifer has been strongly altered due to the groundwater drainage by the mines. Besides the lowering of the water table, changes in groundwater chemistry resulted from the oxidation and hydrolysis of minerals, have developed in the mine workings. After the flooding, further changes of chemistry have occurred due to the dissolution and flushing of the oxidation products and mine waters. Now, large volumes of highly polluted mine waters are stored in the flooded mine workings. These waters are a threat to the existing surface and groundwaters in the area (Razowska, 1998).

The objectives of this study were to (i) identify the dominant hydrogeological and hydrogeochemical processes operating in the disturbed aquifer and (ii) attempt to predict any quality changes of groundwaters that might be anticipated in the region as the result of groundwater rebound. In order to recognise processes controlling the chemistry of these waters, a detailed study of the geological setting, water circulation and the other environmental factors in this area was carried out. The chemical composition, the origin and the spatial distribution of the polluted mine waters in the Czestochowa region were also analysed.

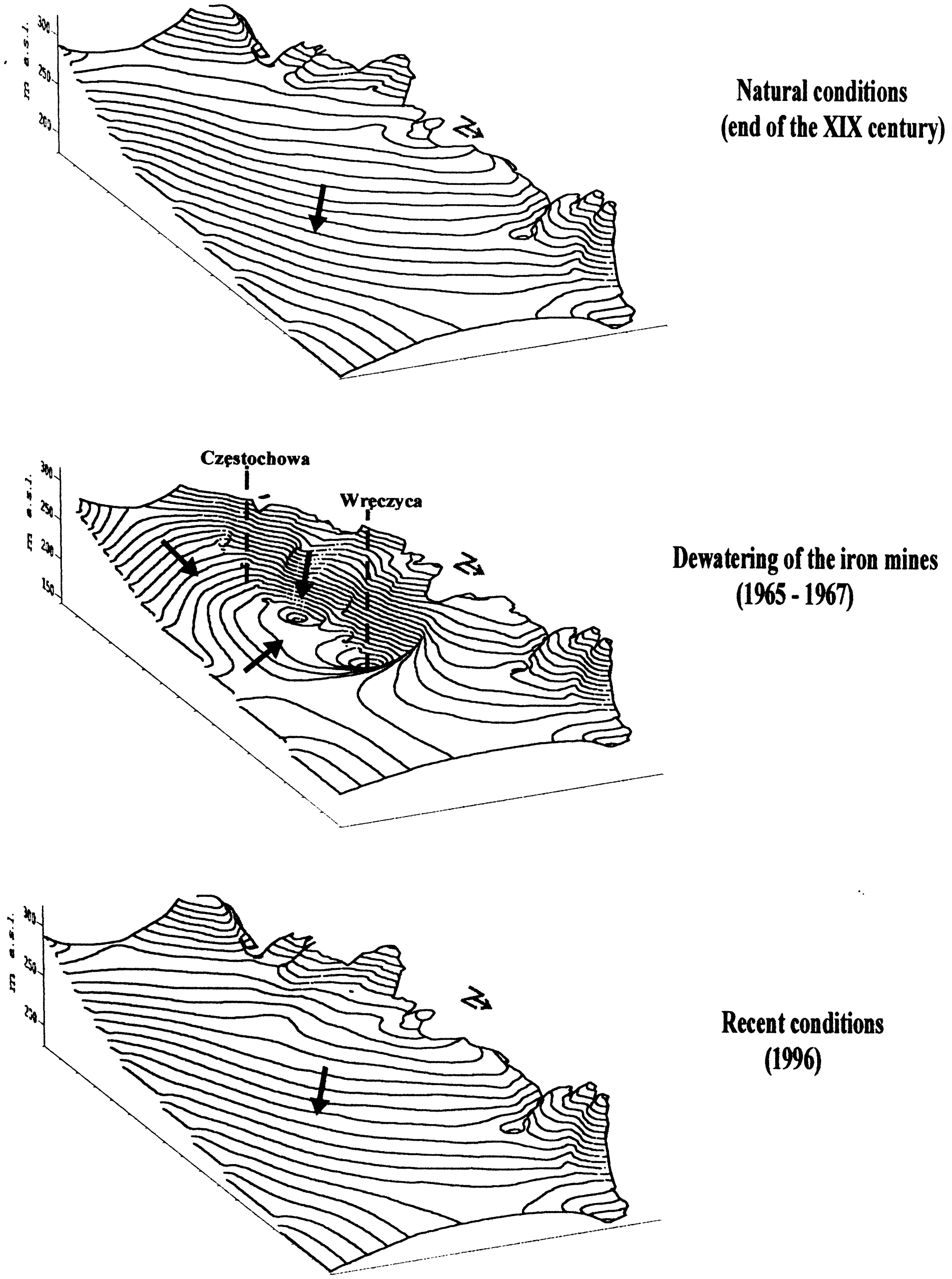
2. Site description

The Czestochowa region, which covers approximately 1500 square km, is a part of the Krakow-Czestochowa Upland located between Zarki and Praszka in the Silesian district (Fig. 1). This region is a part of a large Mesozoic sedimentary basin and the main stratigraphy consists of the Upper and Middle Jurassic sediments, which overlay Triassic deposits (Fig. 1). Iron ores occur in the Middle Jurassic Clay Formation of Bathonian and Callovian age. The main iron-bearing mineral is siderite (Deczkowski, 1976). There are four significant aquifers in the area (Fig. 2B): (1) Quaternary deposits composed of the glacial and fluvial materials; (2) Upper Jurassic limestones; (3) Middle Jurassic sandstones; and (4) Triassic dolomites and limestones (Razowska, Zembal, 1997). The most widespread of these aquifers is the Middle Jurassic aquifer known as “The Koscieliska aquifer” which occurs in the sediments of Aalenian and Bajocian age. This aquifer is mostly confined by the Middle Jurassic Clay Formation of up to 150 m thickness. The aquifer consists of fissured-porous, semiconsolidated, mostly coarse-grained sandstones and sands. Its thickness ranges from 15 to 60 m and the average hydraulic conductivity is 6×10^{-5} m s^{-1} (Hermanski, 1984). This formation extends from the south to the north, and dips to the north–east direction at the angle of 3°. The Koscieliska aquifer has been affected by the iron mining, and all the hydrogeological and hydrogeochemical investigations described in this paper concern this aquifer. The major town in this region, Czestochowa, is a typical urban-industrial town with a population about 250 000. The public water supplies are derived from the Upper and Middle Jurassic aquifers. Both Czestochowa and the smaller town of Klobuck are located along the flow path of the polluted waters, raising concerns that water supplies there may become contaminated by the polluted mine waters in the future.

3. Methods

3.1. Groundwater sampling and analyses

Water samples have been collected since 1991 from the Polish Geological Institute observation wells, water supply wells and flooded mine shafts in the study area (Fig. 2A). A total of 215 water samples were taken (Razowska et al., 1997), pH and Eh (redox potential) were measured in the field along with EC (specific electric conductance) and temperature. Total alkalinity was also measured in the field by acid titration from unfiltered water samples. Groundwater samples were field — filtered through a 0.45 μm filters and filled into acid-washed bottles and acidified. Water samples were analysed for major and minor dissolved chemical constituents (Ca, Mg, Na, K, NH_4, Fe, Sr, As, Ba, Pb, Zn, Cd, Ni, Co, Cu, F, HCO_3, and SiO_2) by atomic absorption spectrometry; SO_4, NO_2, NO_3 and Cl were determined by the ion chromatography. Stable isotopes of oxygen and hydrogen (^{18}O, D) and radioactive isotopes



Natural conditions (end of the XIX century)

Dewatering of the iron mines (1965 - 1967)

Recent conditions (1996)

Fig. 3. Changes of groundwater table of the Koscieliska aquifer in the Czestochowa region. Based on the results of the water flow modelling. Water table countours are drawn at 10 m intervals, and arrows denote directions of groundwater flow.

(tritium and radioactive carbon ^{14}C) were also determined, though isotope samples were collected from selected wells and mine shafts. The chemical analyses were performed in the Central Chemical Laboratory of the Polish Geological Institute in Warsaw. Isotopic analyses were performed in the laboratory of the Faculty of Physics and Nuclear Techniques of the University of Mining and Metallurgy in Cracow. In

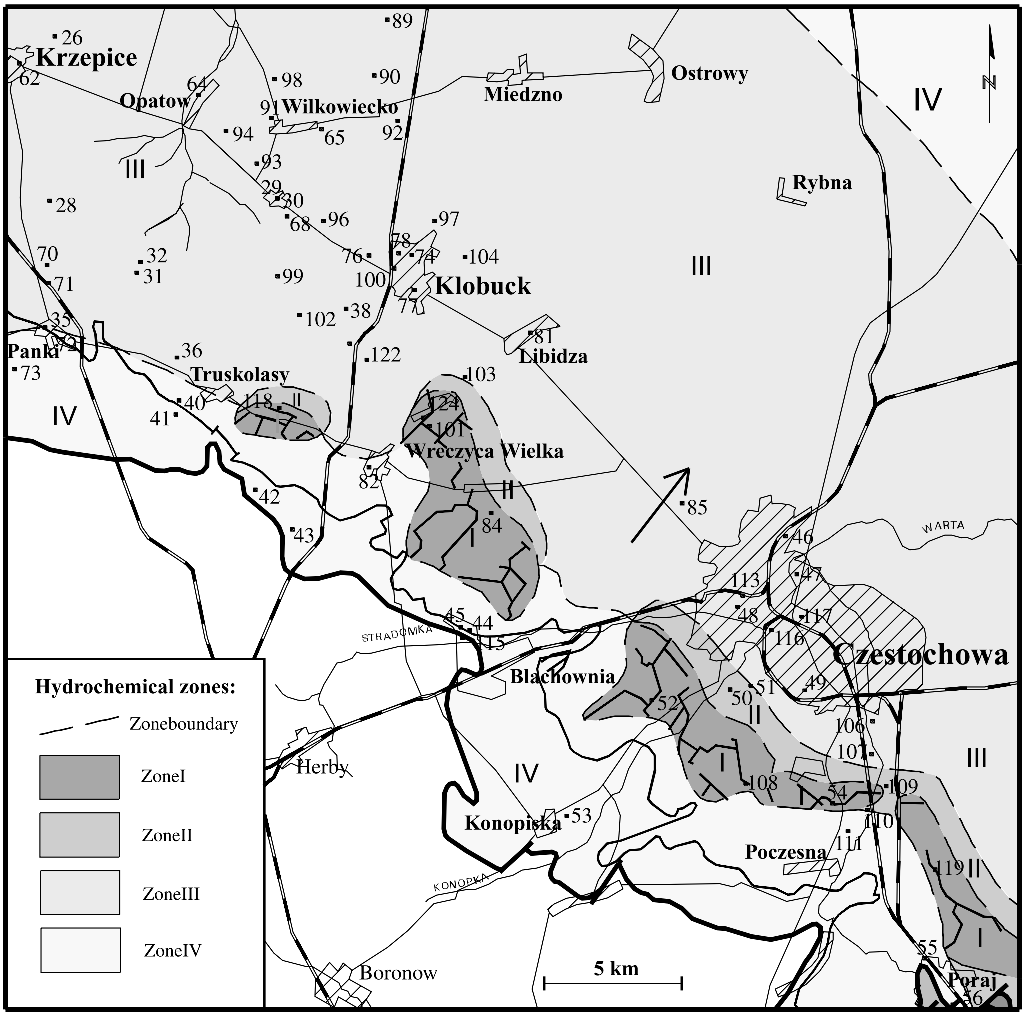


Fig. 4. Hydrogeochemical zonation of the study area. Explanations according to Fig. 2. Arrow denotes the general direction of groundwater flow in the Koscieliska aquifer.

addition, the results of historic water analyses performed by the Czestochowa Geological Works when the iron mines were working and during flooding, have been taken into account in this study.

3.2. Modelling of groundwater flow

A computer model of groundwater flow in the Koscieliska aquifer has been developed. The *SP2H HYDRYLIB* model was chosen as the basis for the numerical modelling because of its ability to solve the changes of groundwater table and because it was available in the Polish Geological Institute (Razowska et al., 1997). The model is based on finite — difference methods. Three hydrodynamic periods have been considered: two verified — the dewatering of the Koscieliska aquifer by the iron mines using the maximum pumping rate from 1965–1967 to the recent years, post-mining conditions, validated for the year 1996. The third was the simulated natural conditions before either the water abstraction or the mine dewatering took place (representing the end of the 19th century). The area which was modelled was 2650 square km and it was divided into 12 800 square cells. The recharge was established from the surface and rivers, the discharge by rivers, by wells and mine dewatering. The piezometric contours in the Fig. 3 depict the results of the simulations. Although the patterns of contours indicate that water flow directions under the current hydrologic conditions are close to those which prevailed prior the pumping, the rising piezometric heads in some observation wells in Czestochowa suggest that the groundwater rebound has not yet been finished there.

3.3. Hydrochemical modelling

In order to study the processes governing the water chemistry in this area, the author performed the calculations using *WATEQ4F*speciation model (Ball and Nordstrom, 1992). The model was based on the data from the field measurements of pH, Eh, temperature and EC and the results of chemical analyses. Principal aqueous species of Ca, Mg, Na, K, Fe, Mn and Zn were predicted for the waters in each zone as well as the saturation indices (SI). The model uses the Davies equation and the extended Debye–Huckel equation to calculate activity coefficients. It solves a set of non-linear mass action and mass balance equations using the continuous fraction iteration. A thermodynamically database which contains the components considered in this study is available within the program.

3.4. Isotope dating of groundwater

Tritium (^{3}H), the radioactive isotope of hydrogen with a half-life of 12.38 years and radiocarbon (^{14}C) with a half-life 5730 years have been used to determine groundwater ages. The groundwater age by ^{14}C was calculated using the equation (Zuber, 1986): $\text{Age} = 8300 \times \ln(c_0/c)$, where $c_0 = 100 \times {}^{13}\delta\text{C}/-25$ (initial activity) and c is the ^{14}C activity (pmc). Post-1953 precipitation often has a ^{14}C activity higher than 50 pmc and contains ^{3}H levels generally above 10 TU (Mayo et al., 1992).

3.5. Statistical methods

The verified analytical and field data for every sample site have been input to the Polish Geological Institute hydrogeochemical spatial database (based on the ARC/INFO GIS) for permanent storage, retrieval and analysis. All the data is kept in 16 information layers. For the modelled data spatial distribution and interpolation Golden Software SURFER was used, and the Linear Regression analysis and correlations between anions and cations were performed using program STATISTICA.

4. Results

4.1. Groundwater chemistry

Considering the impact of the flooded mines on groundwater chemistry, four distinct hydrochemical zones of the Koscieliska aquifer were identified (Fig. 4). These are: *Zone I* — located within the iron mine workings where changes of water chemistry are the greatest. Groundwater in this zone has very high concentrations of total dissolved solids (TDS), especially Fe^{2+}, SO_4^{2-}, Mn^{2+}, Sr^{2+}, Ni^{2+}, HCO_3^-, Ca^{2+}, Mg^{2+} and Na^+. *Zone II* — located outside the mined area but in the immediate vicinity of mines and along the flow path of the polluted waters. High concentrations of TDS appeared later in this zone, and are still lower than in the Zone I. This is a zone of mixing between the mine altered waters and natural waters. *Zone III* — located within the maximum extent of the cone of depression which resulted from dewatering and along the flow path of the polluted waters. The concentration of identified compounds in this zone are at background levels (natural). Most of the municipal and industrial water supplies of the region are located within this zone. *Zone IV* — this is the area beyond the mine drainage influence (outside of the maximum extent of the cone of depression). The chemistry of groundwater of the Koscieliska aquifer is natural here.

In order to evaluate the extent of changes of groundwater chemistry, which have occurred in the Koscieliska aquifer, the modern background concentration of ions and EC can be compared with these in the mining area. The Zones III and IV were taken into account as the chemistry of these waters have not been affected by the mine drainage (Table 1). Groundwaters from the Zones III and IV have low TDS generally below 500 mg l^{-1}. The range of pH values (6.1–7.8) indicate weakly-acidic to weakly-alkaline conditions. Sulphate contents range from 3 to 22 mg l^{-1}, and iron from 0.2 to 5.7 mg l^{-1}. Iron is

Table 1

Average and extremal values of the concentration of the selected ions, pH and electrical conductivity (EC) of waters in the hydrogeochemical zones in the Koscieliska aquifer (1994–1996)

	pH	Ion concentrations (mg/l)									EC (μ S/cm)
		HCO_3^-	SO_4^{2-}	Cl^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	Mn^{2+}	Fe_{og}	
Zone I											
Average	6.60	179.48	688.46	6.57	162.29	52.37	6.07	5.84	3.61	106.32	1316.4
Minimum	5.94	135.371	37.20	3.15	48.20	5.50	2.50	2.07	0.603	8.89	330.0
Maximum	6.89	264.60	1103.00	13.20	245.90	82.02	9.40	13.50	6.612	271.37	1950.0
Zone II											
Average	6.64	193.88	204.54	8.02	86.32	19.98	4.73	3.44	0.87	22.61	606.8
Minimum	5.98	72.44	4.98	1.47	18.00	3.07	1.60	1.20	0.067	6.14	135.0
Maximum	6.97	393.90	779.00	29.50	261.60	72.98	11.10	7.61	2.576	52.62	1640.0
Zone III											
Average	6.95	126.76	9.75	3.92	34.67	4.65	2.99	2.55	0.16	3.36	217.2
Minimum	6.20	72.99	2.64	0.00	13.40	1.03	1.20	1.10	0.002	0.03	114.0
Maximum	7.80	239.81	42.40	37.90	81.50	12.02	10.70	8.10	1.000	10.04	466.0
Zone IV											
Average	6.87	100.84	17.71	15.38	36.65	5.55	6.10	3.17	0.11	1.81	254.7
Minimum	6.14	5.74	1.73	1.11	7.45	2.24	2.20	0.00	0.003	0.05	90.0
Maximum	7.69	244.11	45.00	55.10	84.80	10.99	17.00	12.70	0.338	5.74	480.0

the only compound in the water with concentrations that exceed the acceptable level for drinking waters in Poland (0.5 mg l^{-1}). Ion concentrations in groundwaters from the Koscieliska aquifer in the zones that have been impacted by mining (I and II) are much higher than in the zones of the natural waters (Table 2). Average sulphate concentration in the flooded mines is about 700 mg l^{-1} and the concentration of bicarbonate is about 200 mg l^{-1}. Among cations the highest is calcium content − about

Table 2

Results of the chemical analyses in the zones of the chemical changes (I and II) within the Koœcieliska aquifer (1996). MS — mine shaft, W — well, OW — observation well

Number (Fig. 4)	Eh (V)	pH	Ion concentrations (mg/l)									EC (μ S/cm)
			HCO_3^-	SO_4^{2-}	Cl^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	Mn^{2+}	Fe_{og}	
Zone I												
52 MS	−0.08	5.94	189.0	953.0	6.78	202.3	98.58	7.29	4.18	8.677	78.13	1765
54 W	−0.19	6.58	135.4	265.0	3.15	61.4	13.07	2.51	2.07	1.000	70.14	652
108 MS	−0.08	6.58	172.6	924.0	5.52	208.7	64.33	5.64	5.09	3.609	143.34	1696
118 MS	−0.16	6.89	264.6	1103.0	7.78	222.1	61.86	7.54	7.85	6.612	271.37	1950
119 MS	−0.18	6.58	187.2	528.0	13.20	147.4	41.24	9.40	5.80	2.122	76.75	1124
123 MS	−0.17	6.80	150.9	37.2	6.03	48.2	5.50	2.50	2.40	0.603	8.89	330
124 MS	−0.19	6.85	156.7	1009.0	3.53	245.9	82.02	7.60	13.50	2.624	95.64	1698
Zone II												
50 W	−0.09	6.75	98.8	118.0	2.95	33.1	6.54	2.63	1.58	0.695	38.39	383
51 W	–	5.98	72.4	4.98	1.47	18.0	3.07	1.60	1.20	0.194	6.14	135
56 W	–	6.57	219.5	60.4	29.50	79.6	7.80	11.10	1.70	0.816	7.82	544
109 OW	−0.17	6.91	393.9	779.0	3.72	261.6	72.98	5.36	7.61	2.576	56.62	1640
110 OW	−0.08	6.97	184.8	60.3	2.48	39.3	9.50	2.98	5.10	0.067	4.07	332

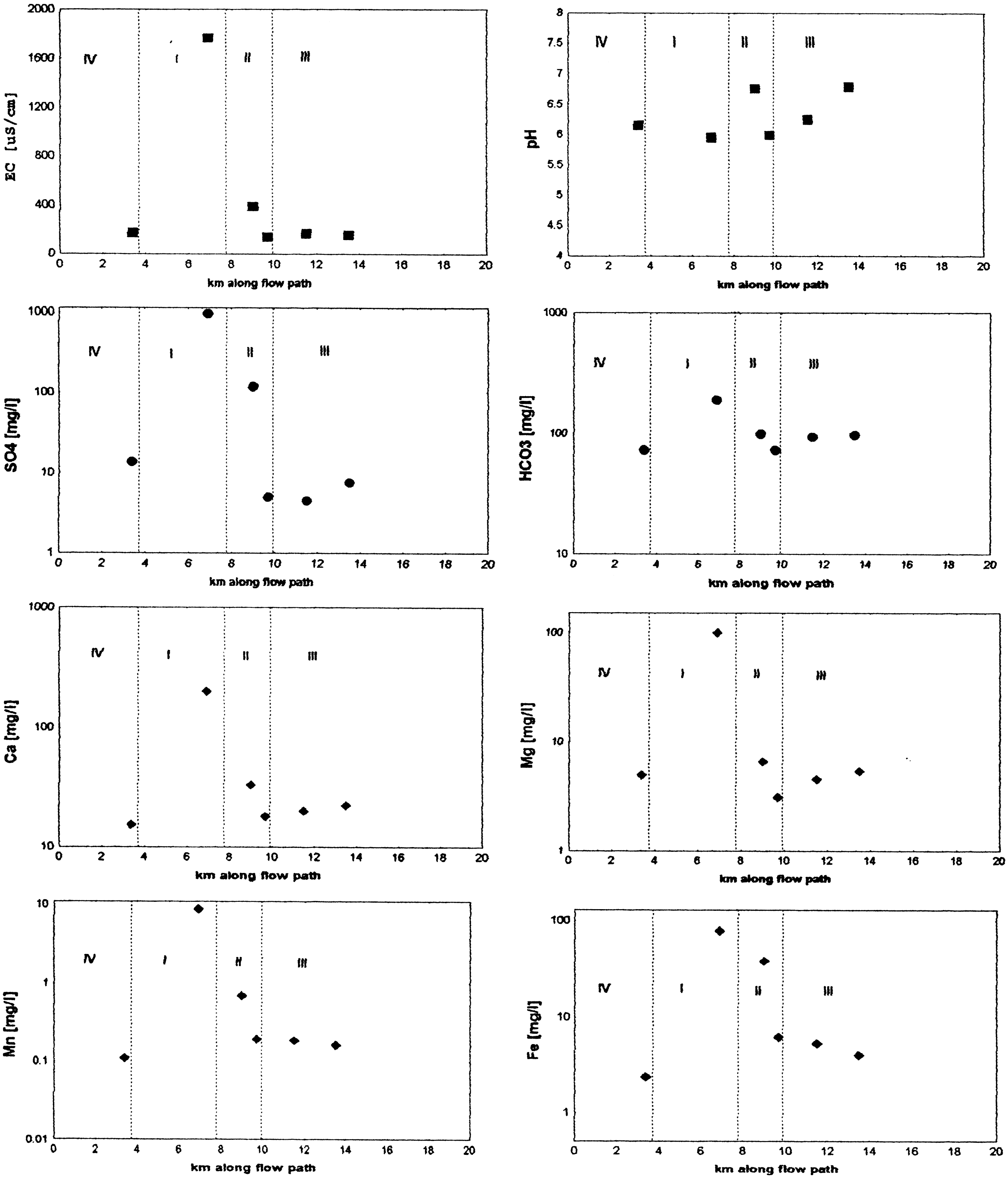


Fig. 5. Variations of the concentration of selected ions, pH values and electrical conductivity of water from the Koscieliska aquifer along the flow path. Flow path according to the hydrogeological cross-section(Fig. 2B). Dashed lines indicate boundaries of I, II, III and IV hydrochemical zones.

Table 3
Distribution of the major species of Ca, Mg, Na, K, Fe, Mn, Sr, Zn and Ba in groundwaters from the Koœcieliska aquifer. Calculated using *WATEQ4F*

Species	Zone I (%)	Zone II (%)	Zone III (%)	Zone IV (%)
Ca^{2+}	75	90	100	100
$(CaSO_4aq)^0$	25	10	0	0
Mg^{2+}	70–80	90–98	100	100
$(MgSO_4\ aq)^o$	20–30	2–10	0	0
Na^+	100	100	100	100
K^+	100	100	100	100
Fe^{2+}	65–75	65–75	75–90	75–90
$FeHCO_3^+$	10–15	10–15	10–15	10–15
$(FeSO_4aq)^o$	10–20	5–10	0	0
$Fe(OH)_2^+$	2–5	2–5	5–10	5–10
Mn^{2+}	70–80	75–95	90	90
$MnHCO_3$	10	10	10	10
$(MnSO_4aq)^o$	20–30	5–7	0	0
Sr^{2+}	75–90	85–95	100	100
$(SrSO_4aq)^o$	5–25	5–25	0	0
Zn^{2+}	60–70	60–90	85–90	85–90
$ZnHCO_3^+$	10–15	3–10	3–10	3–10
Ba^{2+}	50	75–95	95–100	95–100
$(BaSO_4aq)^o$	50	5–25	0–5	0–5

160 mg l^{-1}. Average magnesium content is 50 mg l^{-1}, iron 105 mg l^{-1} and manganese 3.5 mg l^{-1}. Sulphate, iron and manganese contents exceed the acceptable limits for drinking water in Poland, which are: 200, 0.5 and 0.1 mg l^{-1}, respectively. Although the high concentration of heavy metals were expected in this zone, only nickel content (1.62 mg l^{-1}) exceeds the Polish drinking water limit of 0.03 mg l^{-1}. The concentrations of Zn, B, Co and Li are higher than background values, but do not exceed limits for drinking water. In Zone II the highest cation concentrations are iron (23 mg l^{-1}) and manganese (1 mg l^{-1}). Along groundwater flow path (Fig. 5) concentrations of all ions decrease with distance from the flooded mines. The water types are different in these zones. In the zones of natural waters (III and IV) these are of HCO_3 — Ca type. In the zone of mixing (II) this is HCO_3–SO_4–Ca–Mg and in the zone of the flooded mines (I) of SO_4–Ca–Mg type. Waters from the zone of mines have TDS values ranging from 1000 to 2000 mg l^{-1}, whereas TDS values range from 500 to 1000 mg l^{-1} in the zone of mixing. The waters have values of pH ranging from 5.9 to 6.9, which indicate weakly-acidic conditions. Redox potential of the waters (Eh) range from −0.20 to −0.06 V indicating weakly-reducing conditions.

4.2. Hydrochemical processes

The underground iron mining in the Czestochowa region disrupted groundwater flow patterns and exposed rocks containing iron, zinc, lead sulphides such as pyrite, marcasite, sphalerite, galena and chalcopyrite to the oxygenated environment. Exposed rocks were subjected to oxidation along pores, fractures and mine workings. As a result of the pumping, surface waters infiltrated to the dewatered zone of the Koscieliska strata and the mine workings. Oxidation products such a gypsum, melanterite, epsomite, jarosite, anhydrite, alunite, celestite, calcite, dolomite, magnesite, rhodochrosite, smithsonite, strontianite

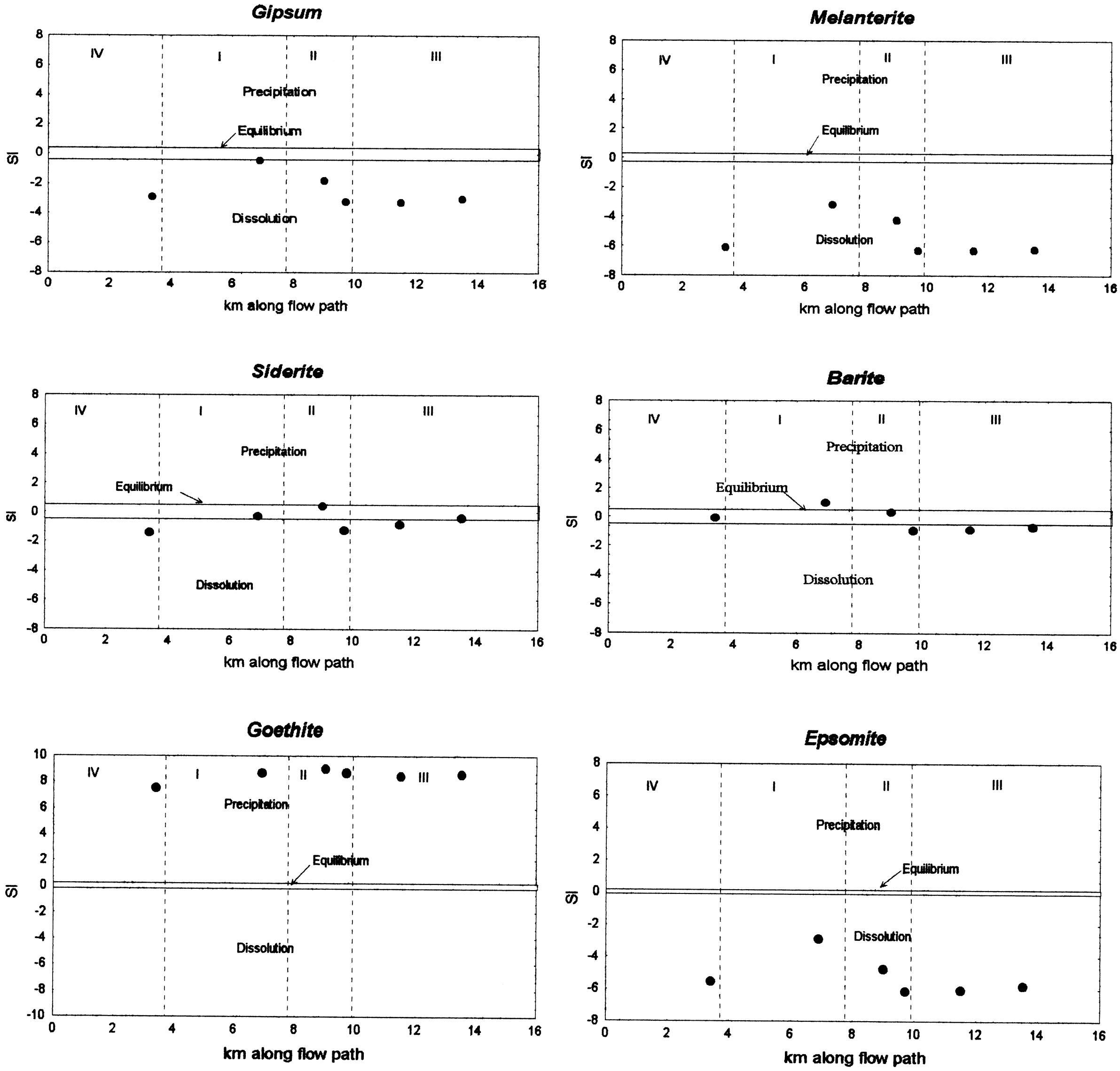


Fig. 6. Saturation Indices (SI) of gypsum, melanterite, siderite, barite, goethite and epsomite along the flow path. Flow path according to the hydrogeological cross-section (Fig. 2B). Calculated using *WATEQ4F*. Dashed lines indicate hydrogeochemical zone boundaries.

and witherite precipitated in the dewatered zone. As flooding occurred, these highly soluble minerals dissolved, and this resulted in the production of waters rich in sulphate, iron, manganese, calcium and magnesium contents. These processes may be described by the reactions (Younger, 1998):

$$FeS_2 + H_2O + 7/2O_2 \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1)$$

$$Fe^{2+} + SO_4^{2-} + 7H_2O \rightarrow FeSO_4^{2-} \cdot 7H_2O \quad (2)$$

The dissolution of these oxidation products caused the release of hydrogen ions and consequently the decrease of the pH of these waters. This resulted in the production of the acid mine drainage (AMD) (Barnes and Clarke, 1964). Acidity was neutralised then by the interaction with the carbonate minerals and pH values increased to 6–7. The reactions 3 and

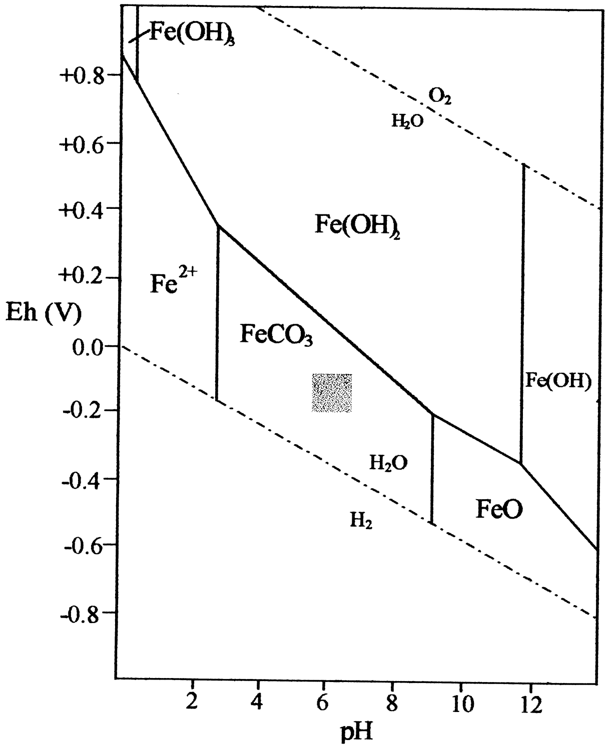


Fig. 7. Stability fields of iron: oxides, sulphides and carbonates in mine waters in the Czestochowa region, constructed by the author. Concentrations: $SO_4^{2-} = 10^{-2}$ mol/l, $H_2S = 10^{-6}$ mol/l. Temperature = 11°C. Grey rectangle indicates the range of measured pH and Eh values in the flooded mines area.

4 show the dissolution of siderite and rhodohrosite

$$FeCO_3 + 2H^+ + \rightarrow Fe^{2+} + CO_2^{2-} + H_2O \qquad (3)$$

$$MnCO_3 + 2H^+ + \rightarrow Mn^{2+} + CO_2^{2-} + H_2O \qquad (4)$$

Despite the neutralisation, ion contents in groundwater within the zone of the flooded mines remain high. These are neutral polluted mine waters with high sulphate, iron and manganese concentrations compared to the background contents in this aquifer (Razowska, 1998). These processes were also described by Younger (1998) and Hedin et al. (1994), who called these waters: "net-alkaline". Role of bacteria during the formation of these waters is also important. The oxidation of ferrous sulphide to ferric sulphate is accelerated by sulphide-oxidising bacteria, as well as the high concentrations of sulphate in these waters may persist due to Fe^{3+}-reducing bacteria which cause the exclusion of sulphate reduction (Chapelle and Lovley, 1992).

The species concentrations calculated by *WATEQ* are different in each hydrochemical zone; in the zones of the neutral polluted mine waters and the mixing zone, more species appear than in the Zones III and IV (Table 3). Cation complexes with SO_4 in the polluted water zones were predicted as a result of the release by the dissolution of sulphate minerals (oxidation products). Ferrous iron (Fe^{2+}) is dominant in these waters as the result of the dissolution of iron sulphates and carbonates and the reduction of ferric iron.

WATEQ was also used for the calculation of the saturation indices (SI) for these minerals, which are significant for the chemistry of waters in the study area (Razowska, 1998). In the Zones III and IV, the model predicts that groundwater is undersaturated with respect to gypsum, with SI values less than zero indicating tendency to dissolution (Fig. 6). In

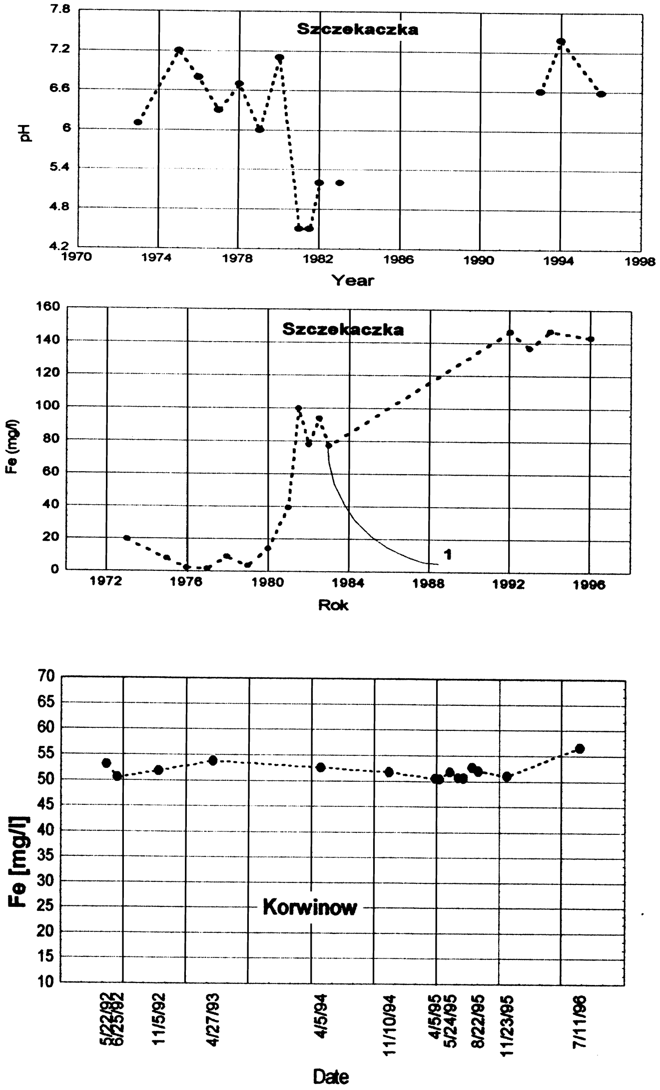


Fig. 8. Variations of pH and Fe_{total} concentrations over the time in waters from Szczekaczka iron mine (108) and Korwinow well (109). 1 — line of the predicted (by Hermanski, 1984) decrease of the iron ions content.

the zone of flooded mines, SI values for gypsum are close to zero indicating saturation with respect to this mineral. This implies that gypsum is one of the mineral phases controlling groundwaters chemistry in this zone. Carbonate equilibrium in the zone of mines is most likely controlled by the siderite ($FeCO_3$). Predicted SI of siderite is approximately equal to zero, which indicates the saturation of these water with respect to this mineral phase. In Zones II and III, the equilibrium state dominates as well, whilst in Zone IV dissolution of siderite is most likely as SI is −1.4 there (Razowska, 1998). Besides siderite, iron concentrations are correlated with iron oxides and hydroxides with the tendency to precipitation (e.g. goethite) (Fig. 6).

The stability fields for iron oxides, sulphides and carbonates in the polluted mine waters, calculated by the author, are shown in Fig. 7. For the pH range from 6 to 7 and from Eh −200 to −60 mV siderite is the stable species of iron

Table 4
Results of the isotopic investigations of groundwaters from the Koscieliska aquifer in the Czestochowa region. MS — mine shaft, W — well, OW — observation well

Number (Fig. 4)	Depth to the aquifer (m)	Tritium (TU)	^{14}C (pmc)	^{13}C (PDB)	Description of the age of water
52 MS	35.6	7.8	34.3	−18.0	mixed
119 MS	83.3	34.4	38.2	−12.5	mixed
123 MS	76.0	39.2	62.5	−14.2	modern
108 MS	72.4	15.7	16.6	−12.5	mixed
54 W	66.0	4.3	25.5	−18.5	mixed
109 OW	136.0	6.3	25.2	−13.7	mixed
50 W	102.0	2.4	33.0	−14.4	mixed
107 OW	79.2	0.0	30.4	−17.1	Early Holocene
106 OW	80.8	0.6	25.0	−17.1	Early Holocene
113 W	148.0	0.2	33.0	−16.5	Early Holocene
47 W	209.0	0.0	3.3	−16.0	Late Pleistocene
46 W	217.0	0.0	7.6	−14.6	Late Pleistocene

which supports the results obtained from *WATEQ* calculations.

4.3. Spatial–temporal analysis of groundwater chemistry

After the flooding, when the equilibrium was approached in mine waters, some physical processes such as a flushing (Frost, 1979) should influence the geochemical evolution of these waters causing the decrease of the ion concentrations. This was suggested by Hermanski (1984) who predicted that Fe concentrations in the "Szczekaczka" mine should have decreased over the time and reached values of the background after 7–8 years. Now, fifteen years after the flooding of the Szczekaczka mine, the iron content is still very high (150 mg l^{-1}) as well as sulphate content (1100 mg l^{-1}) (Fig. 8). The flushing is insignificant due to very low flowing rates occurring after the rewatering the aquifer. The hydraulic gradients in the Koscieliska aquifer, obtained from the modelling are low (Razowska et al., 1997) and range from 0.002 to 0.009. The estimated flowing rates of the polluted waters from the flooded mines are low and range from 3 to 6 m yr^{-1}. Basing on the recharge rate, permeability and hydraulic conditions at the boundaries of the mined system, the residence time of polluted minewater in the flooded mines was estimated from 300 to 500 years (Razowska, 1998).

This has been confirmed by the spatial–temporal analysis of the selected ion concentrations (Razowska et al., 1997). The observations of the ion contents have been conducted for the last eight years in groundwaters from wells and mine shafts. The results obtained from the statistical analysis have shown that the variations of the ion concentrations are not significant and no trends of increase or decrease have been observed during this period.

4.4. Isotope dating

The results of the isotopic investigations of these waters suggest the possible impact of the mines dewatering on the hydrogeological environment as well as the low flowing rates of groundwater in the Koscieliska aquifer. Groundwater samples from the Zarki region and the recharge areas of the Koscieliska aquifer contain tritium (above 30 TU) and radiocarbon (above 50 pmc) and these waters are defined as modern (Table 4). Groundwater samples from the flooded mine workings and from the Zone II, due to the isotopic discordance (low tritium and high radiocarbon values), are considered mixed. Modern waters recharged after 1953 are mixed with older waters, recharged in the Early Holocene as a result of the disturbance of water flow caused by the pumpage of the iron mines.

Although the Koscieliska aquifer was dewatered by the mine drainage, the age of waters from the Zone III in Czestochowa has been determined as Early Holocene (tritium below 1 TU and radiocarbon around 30 pmc), which strongly suggests that these waters had recharged before the dewatering of the iron mines began.

Water samples from the north–west part of Czestochowa, which do not contain tritium, and have radiocarbon ages ranging from 25 to 17 thousand years, are considered to be of Pleistocene age, and were recharged after the last glaciation. Infiltration during a colder climate is suggested by the lighter stable isotopic composition.

5. Conclusions

The results indicate that the changes of groundwater chemistry in the Koscieliska aquifer within the flooded mine workings are significant. Fifteen years after the flooding of mines, the ion concentrations in the polluted mine waters are much higher than in the background. Maximum SO_4^{2-} contents reach 1103.0 mg l^{-1} and are 6 times higher than the acceptable levels for human consumption of water (Polish Drinking–Water Limits), Mn contents reach 6.61 mg l^{-1} and are 70 times higher, and Fe_{tot} reach 271.4 mg l^{-1} and are 500 times higher.

Water flow modelling and hydrogeochemical interpretations suggest that waters in the Zone III, in spite of their occurrence within the area of the cone of depression caused by the iron mining, are not influenced by the polluted mine waters. This is corroborated by the isotopic investigations. The age of waters from this zone has been determined as Early Holocene, which strongly suggests that these waters had recharged before the dewatering began. The isotope hydrology is a very important method of the study of the rebound of the cone of depression, and it may be useful not only for the validation of hydrochemical modelling, but the age determination may lead to the similar conclusions as the long-term monitoring of changes of water chemistry.

Hydrochemical studies showed that after the flooding the equilibrium was approached in the mine waters. As the flow rates of the polluted waters from the flooded mines are low, the flushing process is insignificant here and therefore the self-cleaning of the polluted mine waters will develop slowly. The results of the hydrochemical studies suggest that waters stored in the mine workings may be defined as quasi-stagnant. Middle Jurassic aquifer water supplies located in Czestochowa are not polluted by mine waters today, but the predicted contamination of waters will occur in the first supplies at the end of the 21st century. However, it may last for 300–500 years. If the formation of the polluted acid and neutral waters, in such mined sedimentary ores as in the Czestochowa region, is not prevented, the residual pollution of groundwaters in the flooded mines may persist for several centuries. This has been confirmed by the spatial–temporal analysis of the ion concentrations as the interpretation of eight years observations of the ion contents in groundwaters from selected wells and mine shafts in all zones have shown no trends of increase or decrease.

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