

RAINFALL POLLUTION AND CARBONATE ROCK SOLUTION WITHIN UPPER JURASSIC KARSTIC AQUIFER IN THE SOUTHERN PART OF CRACOW-CZĘSTOCHOWA UPLAND (SOUTHERN POLAND)

RIEŠENIE VZŤAHU ZNEČISTENIA ZRÁŽOK A ROZPÚŠŤANIA KARBONÁTOVÝCH HORNÍN JURSKÝCH KRASOVÝCH KOLEKTOROV JUŽNEJ ČASTI VYSOČINY KRAKOW-CZĘSTOCHOWA (JUŽNÉ POĽSKO)

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ABSTRACT

The paper presents results of hydrochemical investigations carried on in the nineties within the karstic region of Cracow-Częstochowa Upland, mainly of rural character, which is under anthropopressure from agglomeration of Cracow and Upper Silesia. Progressing acidification of rainfall correlated with decrease of mineralization and calcium and ammonium ion concentration in it was stated. Within vadose zone of carbonate rock massif there is observed change of water pH in buffering process to slightly alkaline, dynamic increase of major elements concentration as result of carbonate rock leaching, slow vertical migration of sulfate and chloride pollution front and biological consumption of nitrate and potassium. Within phreatic zone hydrochemical type of water is changed from $\text{HCO}_3\text{-SO}_4\text{-Ca}$ to $\text{HCO}_3\text{-Ca}$ whereas average sulfate ion concentration is distinctly lower and other major elements one is respectively lower. Within phreatic zone there is observed increase of mineralization of water, increase of Ca, Mg, HCO_3 , SiO_2 , Sr and Ba ion concentration in water in vertical profile and along regional flow direction (E, NE) whereas in the southern part of the Upper Jurassic aquifer – from tectonic horsts toward tectonic troughs. This general tendency can be modified by intermediate and local flow and anthropopressure.

KEY WORDS

precipitation, fissure-karstic water, carbonate rock solution, transformation of water chemistry

KLÚČOVÉ SLOVÁ

zrážky, puklinovo-krasové vody, rozpúšťanie karbonátov, zmena chemického zloženia vody

INTRODUCTION

Cracow-Częstochowa Upland (CCU) situated within upland zone of southern Poland divides into four mesoregions: Częstochowa Upland, Olkusz Upland, Krzeszowice Trough and Tenczynek Horst (Kondracki, 2000). The Upper Jurassic aquifer within CCU was classified as a Main Groundwater Basins (MGWBs), precisely the southern part of MGWB Częstochowa E no 326 (Kleczkowski ed.,

1990). The fissure-karstic-porous Upper Jurassic aquifer is of unconfined character. It occupies area of the Upper Jurassic outcrops covered by Quaternary sediments, locally Tertiary and Cretaceous. The eastern part the aquifer immerses under Cretaceous sediments of Miechów basin. The reservoir rocks are fissured and karstic limestones of thickness from tens to 300 meters. The paper presents changes of precipitation chemical composition during its vertical

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percolation through calcareous massif in Ojców National Park (ONP) area. Moreover process of carbonate rock solving by karstic waters in the regional scale of CCU is presented.

RAINFALL POLLUTION

ONP situated in the southern part of CCU is an area of special values in aspect of nature and landscape in the scale of Poland. Its localization between two urban-industrial agglomerations of Upper Silesia to the west and Cracow to the south-east is the biggest hazard for it. Investigations of precipitation pollution have been carried on in ONP since 1989 (Leśniok & others 2002, Drożdżik 2002).

In the years 1990–2001 no differentiation in sulfate ion concentration in precipitation was observed. Predominated range from 4.1 to 6.0 mg/dm^3 (fig. 1). This fact is connected with permanent high emission of sulfate dioxide from industrial area deposited in a result of rainout in the area of ONP. Average annual SO_2 concentration observed in air around Ojców varies

from 27.2 to 48.2 $\mu\text{g/m}^3$ (tab. 1). Phenomenon of acid rain is additionally enlarged by systematic reduction of dust emission into atmosphere, which alkalizes acid rain water. Average annual suspended dust concentration in air decreased from 26.4 to 11 $\mu\text{g/m}^3$, while precipitation average annual value of electrical conductivity – from 63 to 34 $\mu\text{S/cm}$ (tab. 1, tab. 2). Appropriately observed decreased concentrations of calcium and ammonium. In the years 2000–2001 – 80% of analyzed calcium ion concentrations were in range 0–2 mg/dm^3 , maximally 10 mg/dm^3 (fig. 2). At the same time precipitation pH value ranged from 4.1 to 4.3 (average pH of natural precipitation is 5.1–6.0) (tab. 2). At present nitrate ion concentration in precipitation does not exceed 2.0 mg/dm^3 (fig. 3), while chloride ion concentrations are in range of 2–6 mg/dm^3 . Between 1996 and 1998 average concentrations of strontium and barium ions originating mainly from hard coal and fuels combustion as well as SiO_2 were adequately: 0.002, 0.005 and 0.17 mg/dm^3 (Motyka & others 2002).

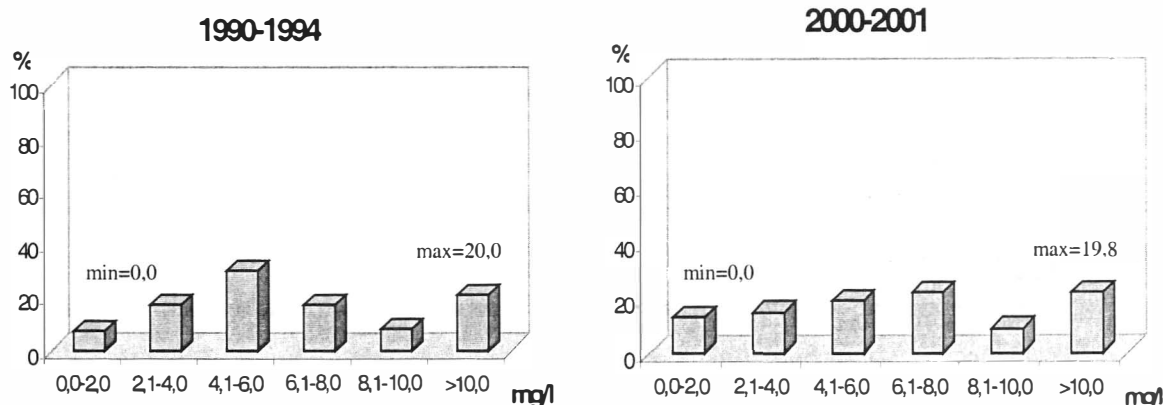


Fig. 1: Distribution of sulphate ion concentration in precipitation in ONP

Tab. 1: Mean annual concentrations of suspended dust and SO_2 in 1990–2001 ($\mu\text{g/m}^3$)

Year	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001
Dust	26,4	21,0	25,6	25,1	21,5	22,5	33,1	30,7	31,6	12,0	13,0	11,0
SO_2	43,8	39,2	36,4	46,2	27,2	28,7	30,8	32,3	33,0	44,3	36,0	48,2

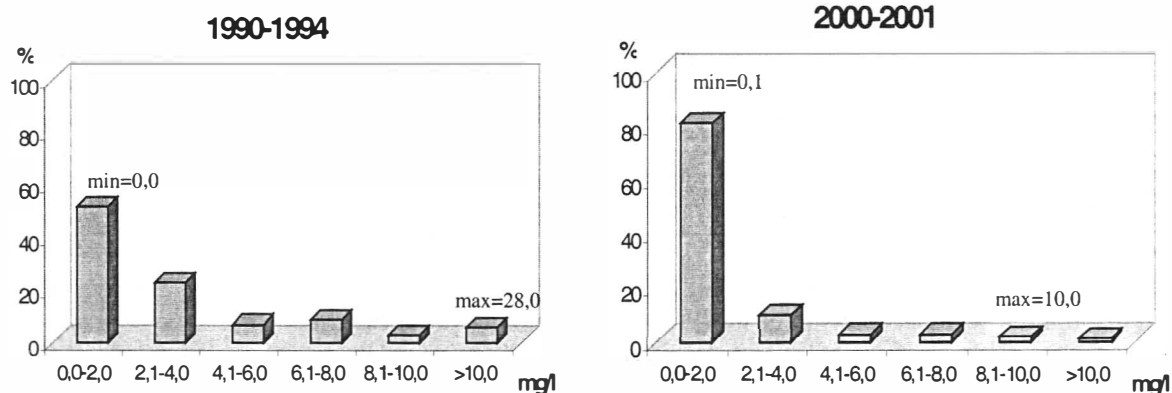


Fig. 2: Distribution of calcium ion concentration in precipitation in ONP

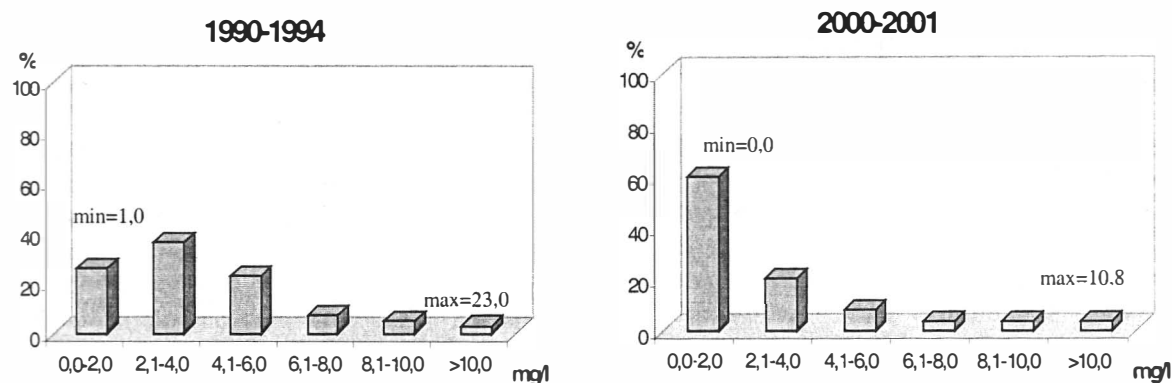


Fig. 3: Distribution of nitrate ion concentration in precipitation in ONP

Tab. 2: Mean annual values of precipitation electric conductivity and precipitation reaction

Year	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001
C_M [$\mu S/cm$]	63,0	61,0	49,0	48,0	46,0	43,0	40,0	35,0	41,0	40,0	40,5	33,6
pH	4,8	5,0	4,5	4,6	4,7	3,7	3,9	4,2	4,1	4,2	4,1	4,3

CHEMISTRY OF VADOSE AND PHREATIC ZONES WATERS

In the years 1996–1998 J. Motyka and others (2002) studied chemical composition changes of precipitation infiltrating through vadose and phreatic zones to surface waters in the area of ONP with special attention to vadose zone, where water was sampled from drippings and water pools in nine caves (mainly from Łokietek and Dark Cave).

Within vadose zone vertical water infiltration takes place mainly through small fractures, subordinately through wide fissures and karstic channels. Long time of water stay in small

hydraulic systems favors increased mineralization.

Process of acid rain water buffering in deeper soil layers and in carbonate rock environment causes change of water pH in caves into slightly alkaline (average value 7.97). It increases considerably: electric conductivity of infiltrating waters, concentrations of major elements as well as SiO_2 , Sr and Ba concentration as a result of carbonate rock leaching. Waters of vadose zone are of HCO_3-SO_4-Ca or SO_4-HCO_3-Ca hydrochemical types, while waters of phreatic zone are almost entirely of HCO_3-Ca type. In phreatic zone pH insignificantly decrease (average value 7.23),

while distinctly lower are average values of Ca, Na (tab. 3). mineralization (C_M) and concentration of SO_4 , Cl,

Tab. 3: Average values of selected elements in infiltration waters of ONP area (1996–1998)

Zone	Element											
	pH	C_M mS/m	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	SO_4 mg/l	Cl mg/l	NO_3 mg/l	Ba mg/l	Sr mg/l	SiO_2 mg/l
Vadose	7,97	62	134	3,9	6,9	1,6	155	22	14,7	0,027	0,091	9,75
Phreatic	7,23	44	98	2,6	4,5	1,7	19,2	11,5	18,1	0,018	0,062	8,8

On the basis of studied element loads analysis was stated that in vertical profile of ONP area vadose zone slow migration of sulfates, subordinately chlorides pollution front introduced into system with precipitation. At the same time nitrates and potassium are consumed in processes within soil.

SOLVING OF CARBONATE ROCKS IN PHREATIC ZONE

Hydrogeological study of fissure-karstic waters in CCU area has been carried on by author since 1988. It includes hydrochemical investigations, study of hydrogeological parameters of Upper Jurassic aquifer, modeling of groundwater circulation conditions and evaluation of groundwater renewal.

Within CCU there is an observed diversified dynamic of carbonate rock solving. This phenomenon is conditioned upon geological structure, aggressiveness of infiltrating waters and anthropopressure. Within Silesia – Cracow monocline there is observed successive subsidence of Triassic, Jurassic and Cretaceous sediments towards NE. In the southern part of Cracow Upland where block tectonics prevails thick clayey Tertiary sediments complex exists in tectonic troughs as an overburden. In phreatic zone predominate aggressive waters (70–80% of population) and saturation index to calcite (SI_c) is usually –0.8 to –0.01. CCU area is of agricultural character and is vulnerable to spatial pollution from agglomerations of Upper Silesia and Cracow.

Alkaline earth metals: strontium and barium commonly as bicarbonate or silica as hydrated silica occur in waters of Upper Jurassic aquifer as a result of percolation throughout subcutaneous karst zone and carbonate rock solving. Concentration of Sr in soils of SW part of CCU ranged from 20 to about 150 ppm, Ba from 5 to 50 ppm while in bottoms of water courses it is: Sr 10–80 ppm, Ba

25–100 ppm (Lis, Pasieczna, 1995). Average amounts of studied elements in limestone are: Sr 400–850 ppm, Ba 90 ppm, Si 3.4% (Polański, 1988). In Jurassic limestone exploited in studied area average content of SiO_2 is from 0.77% to 8.59%, usually not exceeds 2.5%. Ionic radius of strontium is bigger than calcium one and it easier enters into aragonite structure than in calcite one. In diagenesis process aragonite is less stable in environment and it becomes calcite poor in magnesium what can cause strontium concentration. Carbonate rocks contain small amount of barium because of considerable difference of Ca and Ba ionic radii, what makes difficult to Ba to built in into carbonate structure. Significant barium concentrations are connected with silty admixtures and presence of barite (Polański, 1988). In area of Silesia – Cracow monocline barite accompanies mainly paleozoic sediments and Triassic Zn and Pb deposits (Harańczyk, Szostek, 1970).

Average concentrations of selected hydrochemical elements in phreatic waters of moderate climate area are: SiO_2 – 14.3, Sr – 0.245, Ba – 0.017 mg/dm³ while the most frequent values are: Sr – 0.005–0.050, Ba – 0.002–0.010 mg/dm³ (Macioszczyk, 1987). Strontium as a mobile element accompanies calcium during its migration with water instead of barium, which as poorly mobile element is quantitatively subordinate to strontium. Insignificant solubility of minerals containing silica conditions their occurrence in water in subordinate amounts.

Variability of electric conductivity values, major ions: Ca and Mg (as total hardness), HCO_3 and minor elements: SiO_2 , Sr, Ba concentrations in waters of phreatic zone are presented on figures 4 and 5. Generally there is observed increase of soluble element concentrations in direction of regional flow (E, NE) except of the southern part of the Upper Jurassic aquifer – from tectonic horsts towards tectonic troughs. This general tendency can be modified by intermediate and local flows

connected with rivers and their tributaries draining aquifer, as well as by anthropopressure what is

reflected in chemical composition of stream and shallow wells water in rural areas.

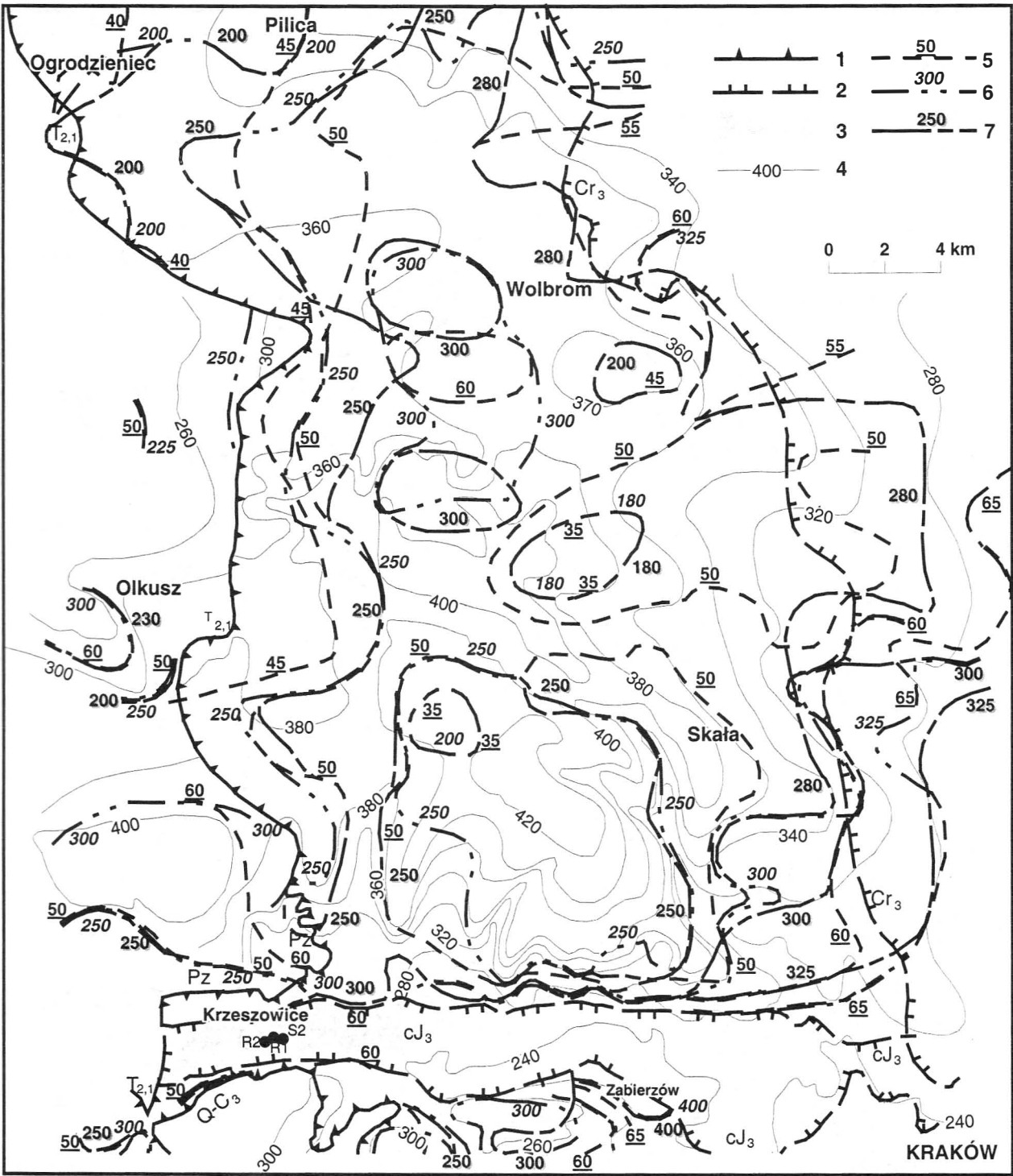


Fig. 4: Variability of electric conductivity, total hardness and bicarbonate concentration in Upper Jurassic aquifer waters in southern part of Częstochowa-Cracow Upland

boundary of Upper Jurassic aquifer: 1 – unconfined; 2 – isolated; 3 – lack of useable aquifer; 4 – groundwater contour (in mg/dm^3); 5 – C_M (mS/m); 6 – T_H ($\text{mgCaCO}_3/\text{dm}^3$); 7 – HCO_3 (mg/dm^3)

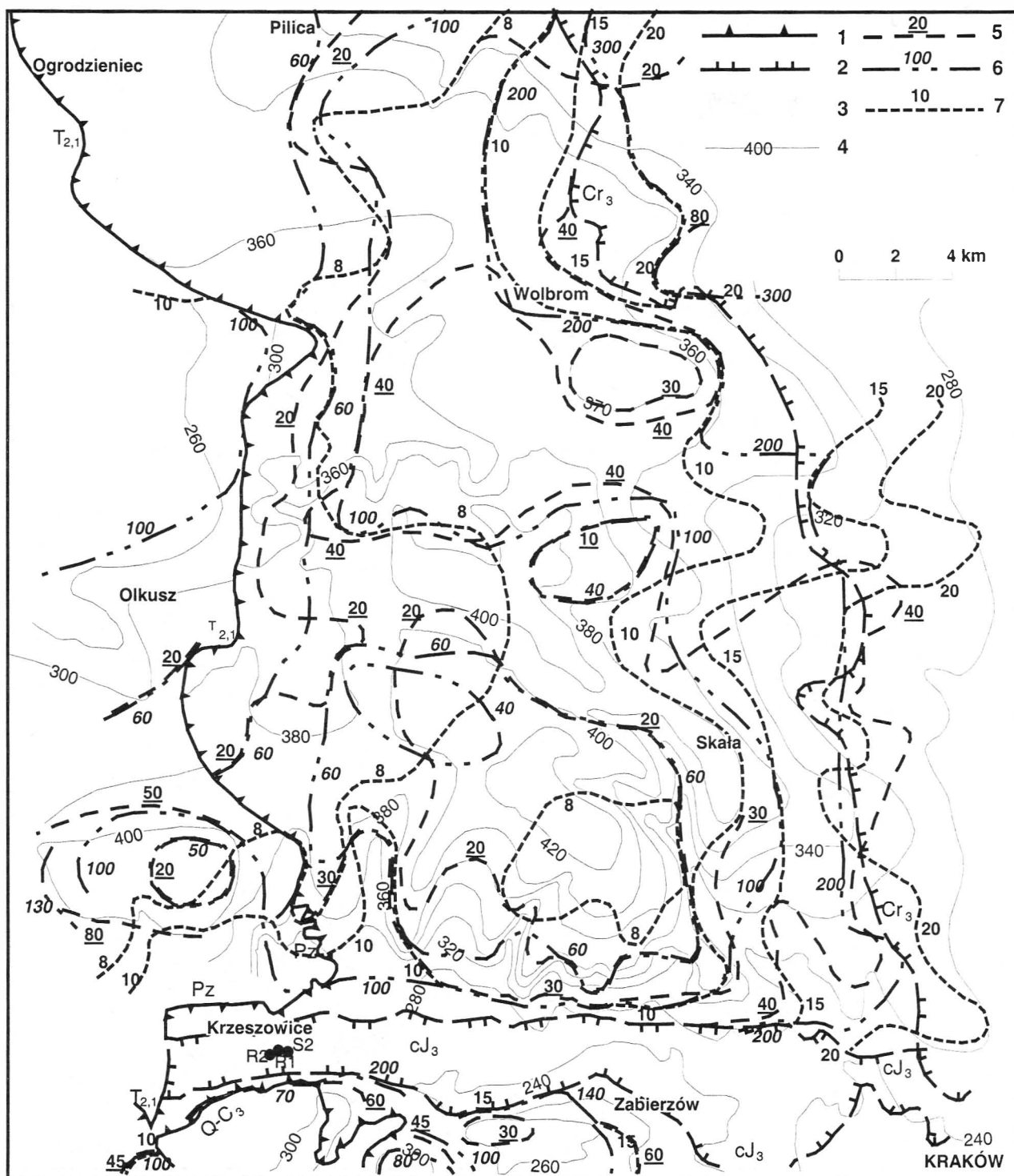


Fig. 5: Variability of strontium, barium and silica concentrations in Upper Jurassic aquifer waters in southern part of Częstochowa-Cracow Upland

boundary of Upper Jurassic aquifer: 1 – unconfined; 2 – isolated; 3 – lack of useable aquifer; 4 – groundwater contour (in mg/dm³); 5 – Sr (mg/dm³); 6 – Ba (mg/dm³); 7 – SiO₂ (mg/dm³)

Within the Upper Jurassic aquifer the lowest values of studied elements concentrations occur along its western boundary. In SW part of CCU, between Ogrodzieniec and Wolbrom Gate these values are as follows: $C_M = 31\text{--}47$ mS/m, $T_H = 135\text{--}260$ mgCaCO₃/dm³, $HCO_3 = 135\text{--}280$, $SiO_2 = 4\text{--}9$, $Sr = 0.028\text{--}0.068$, $Ba = 0.009\text{--}0.022$ mg/dm³. In the southern part of the aquifer between Wolbrom Gate and Krzeszowice Trough these values are modified: $C_M = 36\text{--}54(64)$ mS/m, $T_H = 200\text{--}300(350)$ mgCaCO₃/dm³, $HCO_3 = 195\text{--}330$, $SiO_2 = 5\text{--}9$, $Sr = 0.040\text{--}0.092(0.149)$, $Ba = 0.009\text{--}0.030(0.055)$ mg/dm³. This part of the Biała Przemsza river drainage basin is situated in range of Zn and Pb ore mining activity in area of Olkusz. Disturbance of water flow system appears as intensive percolation of Upper Jurassic aquifer waters into Triassic aquifer, particularly where hydraulic connection between aquifers are convenient, while drainage by rivers is insignificant. Values of specific underground runoff are adequately: 4.2 and 1.1 dm³/s×km (Róžkowski & others, 2001). At the same time there are observed approximate concentrations of studied elements in waters of Triassic aquifer: $C_M = 37\text{--}59$ mS/m, $T_H = 200\text{--}330(370)$ mgCaCO₃/dm³, $HCO_3 = 175\text{--}300$, $SiO_2 = 4\text{--}10$, $Sr = 0.065\text{--}0.109(0.130)$, $Ba = 0.012\text{--}0.031(0.052)$ mg/dm³. Moderate dynamics of carbonate rock solving is observed in areas of watersheds of Olkusz plateau where aquifer recharge is the most intensive (>200 mm/year). Variability of studied elements concentrations is as follows: $C_M = 31\text{--}50$ mS/m, $T_H = 165\text{--}250$ mgCaCO₃/dm³, $HCO_3 = 180\text{--}260$, $SiO_2 = 6\text{--}10$, $Sr = 0.037\text{--}0.065$, $Ba = 0.009\text{--}0.021$ (mg/dm³).

Along the eastern boundary of the Upper Jurassic aquifer and within frontier zone of fissure-porous Upper Cretaceous aquifer recharged laterally by karstic waters can be observed effect of carbonate rock solution resulting from regional flow. It concerns mainly concentrations of $SiO_2 = 15\text{--}28$, $Sr = 0.16\text{--}0.40$, $HCO_3 = 270\text{--}420$ mg/dm³, moderately $C_M = (40)48\text{--}75$ mS/m, $T_H = (240)270\text{--}360$ mgCaCO₃/dm³, $Ba = (0.016)0.030\text{--}0.10$ mg/dm³. Within Tenczynek Horst situated towards south in close vicinity of urban-industrial Cracow agglomeration higher dynamics of carbonate rock solution is observed. In southern direction from

culmination of groundwater table (260–300 m above sea level) towards tectonic troughs Cholerzyn-Pótwieś nad Rybna values of electrical conductivity increase from 48 to 70 mS/m, T_H from 260 to 430 mgCaCO₃/dm³, HCO_3 from 220 to 430, SiO_2 from 10 to 20, Sr from 0.07 to 0.23, Ba from 0.03 to 0.13 mg/dm³.

Maximal concentrations of carbonate rock solved elements were found in an area of Krzeszowice trough where Upper Jurassic aquifer is isolated. In Krzeszowice mineral waters isolated from active circulation zone are exploited. They are chloride waters of joint Cr₁-J₃ aquifer (S–2 well) and sulfate ones occurring in Tortonian strata with gypsum (R–1 and R–2 wells). Chemistry of chloride waters is as follows: total mineralization about 3 g/dm³, $SiO_2 = 22\text{--}26$, Sr about 2.50, Ba do not exceed 0.15 (mg/dm³). Sulfate waters of infiltration origin, probably from climatic optimal season (R–1) and Atlantic glacial period (R–2) are characterized by similar mineralization (2.39–2.68 g/dm³) but significantly higher concentrations of SiO_2 (47–56) and Sr (10.2–13.8) and negligible of Ba (<0.01–0.02) mg/dm³ (Wagner, 2000). Such water chemistry reflects geological structure and conditions of water circulation because content of Sr in gypsum of Fore-Carpathian Depression is high and reaches 0.025–3.6% with average 0.18% (Parafiniuk, 1987).

Similar phenomenon can also be observed in minor scale in an area of southern slope of Olkusz plateau. In karstic, 4 kilometers long, Będkowiec karstic canyon in conditions of local circulation increase of studied elements in waters from initial springs to the northern margin of Krzeszowice trough can be observed in limits: $C_M = 39\text{--}48$ mS/m, $T_H = 225\text{--}270$ mgCaCO₃/dm³, $HCO_3 = 205\text{--}285$, $SiO_2 = 7.5\text{--}8.3$, $Sr = 0.040\text{--}0.084$, $Ba = 0.024\text{--}0.034$ mg/dm³.

In degraded waters exploited by dug wells and drained by springs in rural areas there are observed unnaturally high concentrations of carbonate rock solution indices which are as follows: $C_M = 130$ mS/m, $T_H = 580$ mgCaCO₃/dm³, $HCO_3 = 660$, $SiO_2 = 30$, $Sr = 0.77$, $Ba = 0.11$ mg/dm³.

FINAL REMARKS

Investigations of vertical hydrochemical

zonality in Ojców National Park area have shown that process of acid rainfall buffering in limestone several times increases calcium and sulfate loads in vadose zone. Load of chloride, Sr and silica increases as well. Effect of human impact observed in this area appears as slow migration of water pollution front of sulfate and subordinately chloride.

Within studied carbonate rock environment zonal variability of concentrations mainly of strontium and silica and also HCO_3^- ion is useful index of rock solution dependent on length of groundwater circulation. Values of higher

mineralization and total hardness are more scattered because of local anthropopressure influence. Low concentrations of barium ion, sometimes ambiguous laboratory results, are difficult to comment.

The most intensive process of carbonate rock solving is observed in karstic waters in areas situated close to urban-industrial agglomerations for example in an area of Tenczynek Horst in vicinity of Cracow. Maximal concentrations of studied elements occur in isolated from surface part of aquifer and as well under local human impact.

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RIEŠENIE VZŤAHU ZNEČISTENIA ZRÁŽOK A ROZPÚŠŤANIA KARBONÁTOVÝCH HORNÍN JURSKÝCH KRASOVÝCH KOLEKTOROV JUŽNEJ ČASTI VYSOČINY KRAKOW-CZĘSTOCHOVA (JUŽNÉ POĽSKO)

RESUMÉ

Vysočina Krakow – Częstochowa je situovaná v zóne vysočiny južného Poľska. Predstavuje krasovú oblasť s prevažne čistým prostredím, ktorá je však pod antropogénnym tlakom spôsobeným blízkosťou aglomerácie Krakova a Horného Sliezska. Vrchný jurský zvodnený kolektor v rámci vysočiny Krakow – Częstochova bol určený ako hlavná nádrž podzemnej vody Częstochova. Puklinovo-krasovo-medzizrnný vrchnojurský kolektor má voľnú hladinu podzemnej vody. Zaberá územie vrchnojurských vrstiev prekrytých kvartérnymi sedimentami, lokálne i terciérnymi a kriedovými sedimentami. Východná časť kolektora sa ponára pod kriedové sedimenty kolektora Miechow. Horniny tvoriace zvodnenú vrstvu sú popukané a skrasovatené vápence s hrúbkou od desiatok po 300 metrov. Postupná acidifikácia zrážkovej vody (obr. 1, 2, 3, tab. 1 a 2) bola korelovaná s poklesom mineralizácie a koncentrácií vápnika a amónnych iónov. V nenasýtenej zóne masívu karbonátových hornín boli zaznamenané

zmeny pH vody posunom k slabo alkalickému typu (tab. 3). Bol pozorovaný nárast koncentrácie hlavných prvkov ako výsledok procesu rozpúšťania karbonátov, pomalá vertikálna migrácia chloridového a sulfátového znečistenia a biologická spotreba dusíka a draslíka. V rámci freatickej zóny sa mení hydrogeochemický typ vody z $\text{HCO}_3\text{-SO}_4\text{-Ca}$ na $\text{HCO}_3\text{-Ca}$, kde priemerné koncentrácie síranov sú výrazne nižšie a zároveň bol v rámci freatickej zóny pozorovaný nárast mineralizácie vody, nárast koncentrácie iónov Ca, Mg, HCO_3 , SiO_2 , Sr a Ba vo vertikálnom profile a pozdĺž, regionálneho smeru prúdenia podzemnej vody smerom V, SV, v južnej časti vrchnotriasového kolektora smerom od tektonických hrástí k tektonickým prepadlinám (obr. 4 a 5). Táto hlavná tendencia môže byť modifikovaná lokálnym prúdením a intenzitou antropogénnych vplyvov. Najintenzívnejší proces rozpúšťania karbonátov bol pozorovaný v krasových vodách nachádzajúcich sa v blízkosti priemyslených aglomerácií napr. v oblasti Tenczynek v blízkosti Krakova. Maximálne koncentrácie sledovaných prvkov sa nachádzajú v častiach izolovaných od povrchu kolektora a taktiež lokálne v oblastiach výrazne antropogénne ovplyvnených.

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