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EVALUATION OF HYDROGEOCHEMICAL STABILITY OF JURASSIC WATERS OF LUBLIN COAL BASIN AS THE BASIS FOR USING THEM IN BALNEOLOGY

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OCENA STABILNOŚCI HYDROGEOCHEMICZNEJ WÓD JURAJSKICH LUBELSKIEGO ZAGŁĘBIA WĘGLOWEGO JAKO PODSTAWA ICH WYKORZYSTANIA W BALNEOLOGII

Artykuł prezentuje wyniki hydrogeologicznych badań obszaru Lubelskiego Zagłębia Węglowego, a w szczególności jurajskiego poziomu wodonośnego. Podzielony jest na cztery zasadnicze bloki tematyczne: 1) stratygrafia, tektonika i litologia warstw jurajskich obszaru LZW, 2) dynamika wód podziemnych, 3) skład chemiczny wód jurajskich, 4) warunki hydrogeochemicznej stabilności. Autorka tekstu wskazuje kilka głównych kierunków wykorzystania wód jurajskich w profilaktyce i leczeniu wielu chorób. Wody zawierające znacznie podwyższoną, w stosunku do najczęściej występującej ilość jonów fluoru, pochodzą z jurajskiej formacji geologicznej i znajdują się na znacznej głębokości pod poziomem terenu. Kopalnia węgla kamiennego ujmuje te wody i łączy je ze znacznie zasolonymi wodami karbońskimi. Po wydobyciu na powierzchnię, a następnie wstępnym oczyszczeniu, wody te są odprowadzane systemem rurociągów i rowów do rzeki. Jurajskie wody, zawierające 6–11 mg F/dm^3 zaliczane do nisko zmineralizowanych ze względu na zawartość terapeutyczną fluoru mogą być wykorzystywane w profilaktyce chorób zębów i przyzębia, a także w przypadku leczenia osteoporozy. Ich właściwości mogą być pomocne podczas leczenia, jak również do utrwalania rezultatów zastosowanych metod, na przykład po zabiegach operacyjnych.

Summary

The paper presents the result of hydrogeological studies of Lublin Coal Basin (LCB), particularly at Jurassic level. It is arranged in several parts: 1) stratigraphy, tectonics and lithology of Jurassic system at LCB territory, 2) groundwater dynamics, 3) chemical composition of waters, 4) hydrogeochemical stability conditions. The paper also suggests a few main directions of using the Jurassic waters in prophylaxis and therapy of many diseases. The waters, containing considerably elevated quantities of fluorine compounds come from Jurassic formation lying at the considerable depth. Coal mine joins them with saline Carboniferous waters. After pretreatment, they are discharged to the surface and to the river. Jurassic waters belong to the group of low mineralised waters. They contain 6–11 mg F/dm^3 fluorides. Thus they can be useful in prophylactics of teeth and paradental illnesses, particularly in risk groups. Thanks to, fluorides contained in these waters they can be used during and after treatment and to support surgical operations or rehabilitation effects.

INTRODUCTION

Fluorine belongs to the group of very active chemical elements. It migrates with water through every part of the environment. It also accumulates easily in human and animal organisms or in plants. Considerable amounts of fluorides, which occur in food, come from ground waters. Main natural resources of fluorine compounds are: fluoroapatite $3Ca_3(PO_4)_2{\cdot}CaF_2$, fluorite CaF_2, cryolite Na_3AlF_6, also biotite, hornblende and tourmaline. Ground waters occurring in the areas of active volcanism can also contain high concentration of fluorine (about 80 mg F/dm^3). The presence of fluorides in air or soil is not natural and results from the pollution of the environment due to antropopresion. Fluorides originated from human activity come from metallurgy of steel and aluminium, chemical industry, opencast and deep mining [6].

The main process, which has a great influence on the chemistry of ground waters, is the leaching of mineral compounds from rocks and their transport them with water for short or long distances. In such hydrogeological conditions, every change of physical or chemical water stability brings about the instability of chemical composition of water. Geochemical stability depends on the temperature, pressure, concentration of dissolved solids in water, its ionic strength, pH, Eh, velocity and direction of flow. All these factors influence the presence of many element ions in ground waters. Chemical type of LCB Jurassic waters is HCO_3 - Cl - Na [3].

The aim of this paper is evaluation of chemical stability with its relation to the quantity of mine waters pumped out. The quantity of pumped out water depends on the coal mining technology and the necessity of assuring miners' security. Situation like this causes many hydrodynamic disturbances in geological formations. As a result we can usually observe changes in ground water flow and chemical composition [7].

STRATIGRAPHY, TECTONICS, AND LITHOLOGY OF JURASSIC DEPOSITS IN LUBLIN COAL BASIN

In the Lublin Coal Basin (LCB) area Jurassic deposits lie directly over the Carbon seams. They consist of carbonate layers. The layer's roof monoclinally descend from 200 m to 1000 m under the ground level in the EW direction. Accordingly, the thickness of Jurassic layers is 30 m in the east, 120 m in the centre and 350 m in the west [4].

Jurassic beds are lithologically diversified. Middle Jurassic formation (part SE) is build of conglomerates and sandstone. Close to it are sandstone, mudstone and dolomite limes, up to detritic limes in the NW part. Locally, there are discontinuous layers in the middle Jurassic seam. Formations are fissured and have cavities of a different size. Additionally, Jurassic sediments are cut-of by many faults. That cause local dislocations. The outcrops of these formations are beyond the frontiers of Poland [2, 8].

HYDRODYNAMICS OF THE LCB AREA

Lublin Coal Basin is located in Lublin-Wołyń artesian basin and at Łuków hydrogeological socle. Main direction of groundwater flow in Mesozoic seams of Paleozoic formations, also in Jurassic sediments, which are being discussed here, is SE-NW. There are a few water aquifers in the profile, but Jurassic horizon is

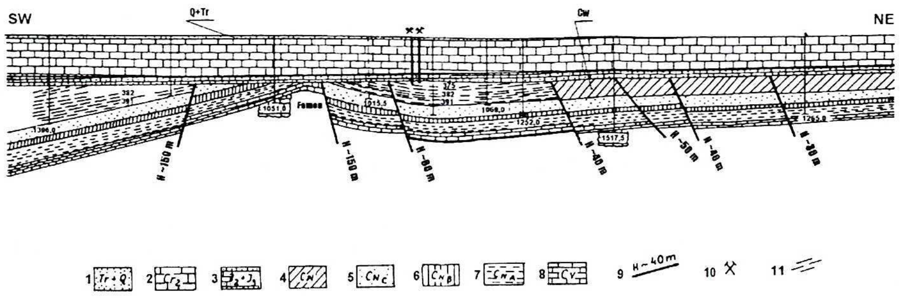


Fig. 1. Lithological - stratigraphical NW-SE cross section of the Lublin Coal Basin
1 - Quaternary and Tertiary formations, 2 - formations of Upper Cretaceous, 3 - Upper and Middle Jurassic, 4 - the younger seams of Westphalian, Lublin beds (West. A and B), 5 - Kumów seams (Namurian C), 6 - Bug seams (Namurian B), 7 - Komarów seams (Namurian C), 8 - Lower Carboniferous formations, 9 - major faults (H - height of the fall throw), 10 - mine shafts, 11 - coal seams. (after Konstantynowicz) [10]

particularly well insulated from the upper and bottom layers especially from the surface. The main direction of the flow depends on hydrostatic pressure gradient. The high territory of Roztocze and Podole gravitational forces flow to NW direction. It is possible to distinguish three water-bearing levels. Jurassic formation is in the middle zone [1–3]. The depth of it varies from 400 to 1100 m under the ground level. Mean filtration coefficient for this formation, depending on the kind of rock kind, range from $4.9 \cdot 10^{-8} \div 6.7 \cdot 10^{-5}$ m/s. Mineralization of these waters is about $0.6 \div 10$ g/dm^3. Hydrogeochemical type of Jurassic waters is Cl - HCO_3 - Na with one specific fluoride ion. The studies carried out in last years show that there are no hydraulic connections between neighbouring seams and the ground surface. Local dislocations, connected with coal mining, have small influence on the flow direction and have no effect on the water quality. Changes of water flow direction are limited only to faults [2, 3, 8].

JURASSIC WATER QUALITY

Mine water analyses were not performed regularly before. Due to enlargement of coal mines „Bogdanka", „Nadrybie", „Stefanów" and depending on the mining, quantities of all water discharged from mines underwent changes. Available chemical analyses show that its ionic composition is stable. The quantity changes of some ions occurring in water are not essential. They result from the reaction with rock in first days of mining and from connecting to new mining walls during next stages. For the security of coal mining it is necessary to uptake the waters occurring in the overlying seams, and to discharge them to the surface. Detailed analyses display the unique chemical composition of these waters, particularly fluoride ion content. Jurassic waters are slightly mineralised with approximately $7 \div 10$ mg F/dm^3. The fluoride to calcium and other ions ratio is characteristic for specific fluoride waters. Occurring at a very big depth, these waters do not contain heavy metals and microorganisms [3].

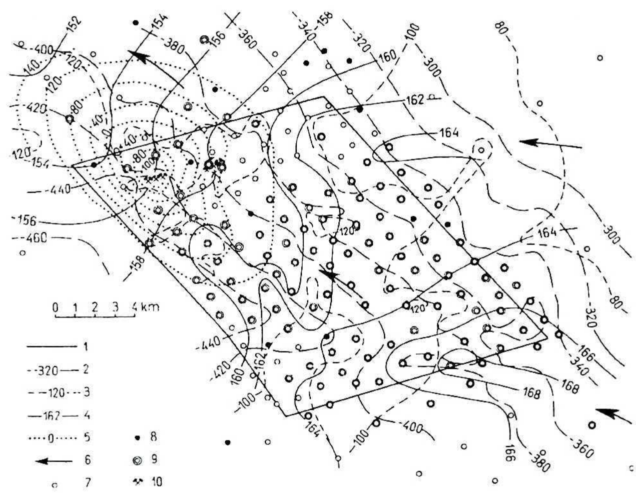


Fig. 2. Hydrogeological sketch of the Jurassic aquifer in the Central Coal District
1 - border of Central Coal District, 2 - isohypses of the Jurassic top (in meters), 3 - isopachytes of the Jurassic formations (in meters), 4 - hydroisohypses of Jurassic aquifer (in meters) under conditions of undisturbed water regime, 5 - hydroisohypses of the Jurassic aquifer under mining drainage conditions, based on piezometric measurements, 6 - flow direction in Jurassic aquifer under undisturbed water regime, 7 - boreholes, 8 - boreholes made for hydrogeological measurements in the Jurassic formations, 9 - boreholes with sandstone recognised in the lower part of Jurassic formation, 10 - mining shafts [7, 8]

Table 1. Concentrations of fluorides in selected regions of Poland [6]

No.	Quantity of fluoride	Region in Poland
	mg F/dm^3	
1	0.5 ÷ 1.0	Warsaw, Mazovian Basin
2	1.2 ÷ 3.2	Gdańsk, Malbork, Tczew (Northern Poland)
3	1.6	Rabka (Southern Poland)
4	2.0	Lubliniec
5	< 5.0	Gdańsk
6	10.0	Lądek Zdrój, Cieplice Śląskie (SW Poland)
7	6 ÷ 11	Lublin Coal Basin (Eastern Poland)

Table 2. Results of a single Jurassic water analysis [3]

No.	Type of analysis		No.	Type of analysis	
1	Temperature °C, K	20. 293	7	Oxygen consumption mg/dm^3	2.00
2	Conductivity S/m	0.16	8	Alkalinity p. mval/dm^3	0.00
3	Colour	4.0	9	Alkalinity m mval/dm^3	8.80
4	pH	8.0	10	Hardness carbonate mval/dm^3	0.84
5	Dry residue mg/dm^3	1025.00		Hardness carbonate °n	2.35
6	CO_2 free mg/dm^3	19.80	11	Total hardness mval/dm^3	8.84
	Cations mg/dm^3			Anions mg/dm^3	
1	Calcium Ca^{2+}	6.40	1	Chlorides Cl^-	297.86
2	Magnesium Mg^{2+}	6.38	2	Sulphates SO_4^{2-}	35.80
3	Iron Fe^{2+}	0.10	3		
4	Sodium Na^+	387.38	4	Bicarbonates HCO_3^-	536.98
5	Potassium K^+	1.14		Fluorides F^-	10.00

In Poland, drinking water quality is defined by special regulations. Below, the regulatory MCL for selected parameters of Jurassic waters is presented:

		MCL (maximum concentration level) for drinking water (less than)	Concentration in Jurassic waters
– Colour	mg Pt/dm^3	20	4
– pH		6.5 ÷ 8.5	8.0
– TDS (total dissolved solids)	mg/dm^3	800	1025
– Hardness $CaCO_3$	mg/dm^3	500	8.84
– Fe^{2+}	mg/dm^3	0.5	1.10
– Na^{2+}	mg/dm^3	200	387.38
– Cl^-	mg/dm^3	300	297.86
– SO_4^{2-}	mg/dm^3	200	35.80
– F^-	mg/dm^3	1.5 more than 0.5	10,00

To conclude, the water of Jurassic origin can be used for drinking, but under control, with regard to fluoride ions. With respect to TDS Jurassic water can be classified to the group of mineral waters. Elevated concentrations of fluorides are valuable as they make it possible to use this water in special forms of therapy [4].

WATER STABILITY

Water analysis carried out since the beginning of coal mining in the Lublin Coal Basin have not been statistically assessed up till now. Calculations made now show stability of all chemical compounds (Tab. 3). Simple diagrams present selected chemical and physical parameters.

Statistical calculation proves that hydrogeochemical characteristics of Jurassic waters from mines of Lublin Coal Basin is stable (Tab. 3). Calculated values of standard deviation, correlation coefficient, variance, arithmetic mean, median value, coefficient of variation confirms this stability.

SUGGESTION FOR USING THERAPEUTIC PROPERTIES OF JURASSIC WATERS

Ground waters owe their therapeutic properties to defined content of microcomponents. These components are presented in quantities, which quality waters as mineral waters. This usefulness depends also on gases, temperature, natural radioactivity or elevated content of one mineral component. Jurassic waters from Lublin Coal Basin contain one characteristic ion, fluorine, which concentration is higher than in other waters in Poland. Ground waters in Poland usually contain 0.2 ÷ 0.5 mg F/dm^3. This is too low regarding the content recommended by physicians for health reasons. According to WHO, the necessary quantity is about 1.0 ÷ 1.5 mg F/dm^3 in drinking and tap water, which complies with Polish Standards. Jurassic waters from Lublin Coal basin contain 6.0 ÷ 11.0 mg F/dm^3. The origin of fluorides is of interest here. To find it out we have to analyse geological and mineralogical cross-section of Jurassic sediments that are built of malm limestone. This formation is fissured and cavited. Fluoroapatites, phosphorites and fluorite fill many of these empty spaces. Flowing water dissolves the minerals and this is the major source of fluoride ions in water [6].

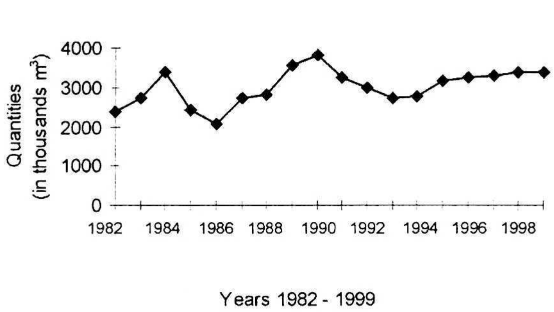


Fig. 3. Quantities of Jurassic waters pumped up from Lublin Coal Basin [2]

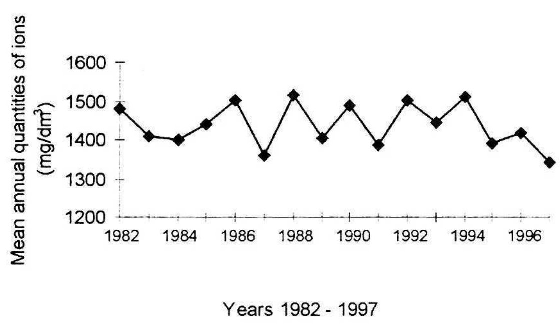


Fig. 4. General mineralization of Jurassic waters [2]

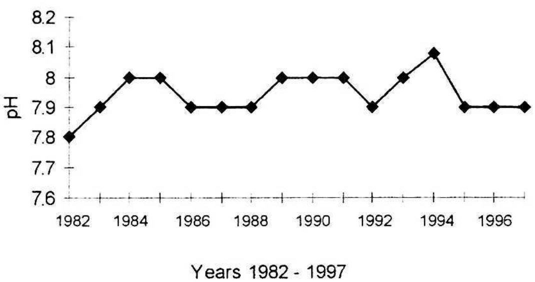


Fig. 5. pH values of Jurassic waters [2]

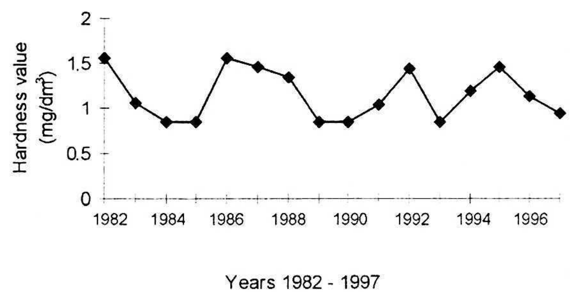


Fig. 6. Hardness of Jurassic waters from LCB [2]

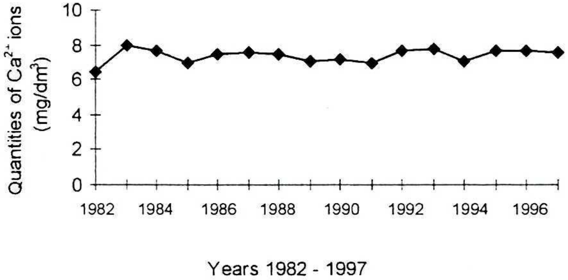


Fig. 7. Ca^{2+} ions concentration in Jurassic waters from LCB [2]

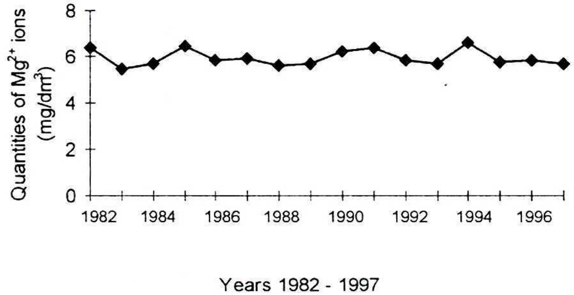


Fig. 8. Mg^{2+} ions concentration in Jurassic waters form LCB [2]

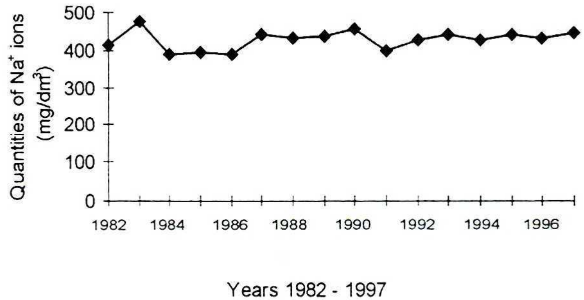


Fig. 9. Na^{+} ions concentration in Jurassic waters from LCB [2]

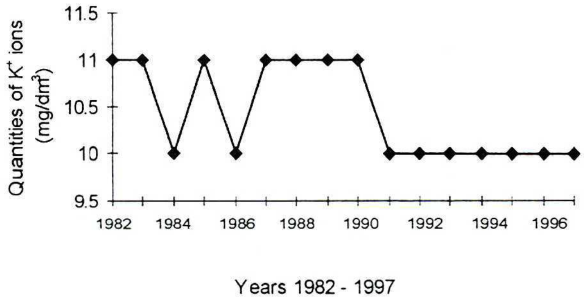
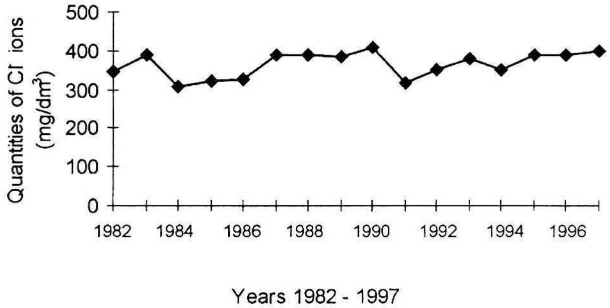
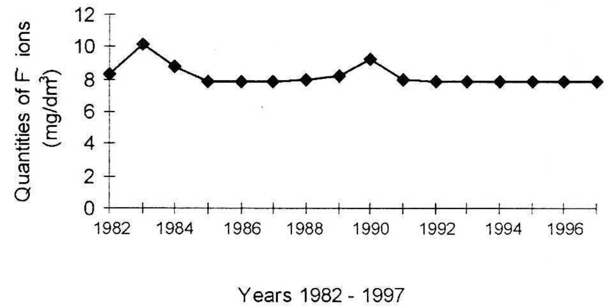


Fig. 10. K^{+} ions in Jurassic waters from LCB [2]


Quantities of Cl⁻ ions (mg/dm³)
500
400
300
200
100
0
1982
1984
1986
1988
1990
1992
1994
1996
Years 1982 - 1997


Quantities of F⁻ ions (mg/dm³)
12
10
8
6
4
2
0
1982
1984
1986
1988
1990
1992
1994
1996
Years 1982 - 1997

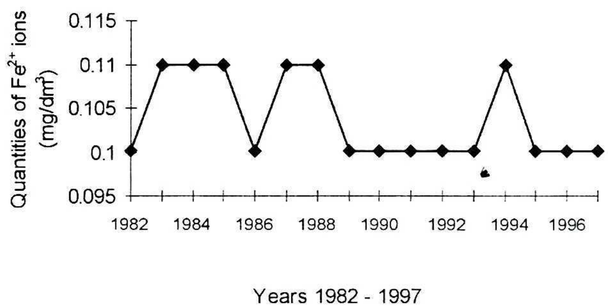

Quantities of Fe^{2+} ions (mg/dm³)
0.115
0.11
0.105
0.1
0.095
1982
1984
1986
1988
1990
1992
1994
1996
Years 1982 - 1997

Table 3. Values of calculated selected parameters of Jurassic water from LCB

Value	Quantities of water	Minera-lization	pH	Hardness	Ca^{2+}	Mg^{2+}	Fe^{2+}	Na^{+}	K^{+}	Cl^{-}	SO_4^{2-}	HCO_3^{-}	F^{-}
	thousands m^3	mg/dm^3		mg/dm^3	mg/dm^3	mg/dm^3	mg/dm^3	mg/dm^3	mg/dm^3	mg/dm^3	mg/dm^3	mg/dm^3	mg/dm^3
Mean	2956.32	1437.01	7.94	1.15	7.36	5.95	0.10	428.64	10.44	364.91	40.71	665.25	8,18
SD	465.38	56.45	0.07	0.28	0.41	0.35	0.01	25.16	0.51	32.89	3.99	48.42	0.65
Variance	216582.6	3187.14	0.01	0.08	0.17	0.12	2.5E-05	632.78	0.26	1081.65	15.93	2344.41	0.42
Median	2917.00	1429.05	7.90	1.10	7.52	5.83	0.10	433.55	10.00	383.15	40.66	686.23	7.86
Correlation coefficient		0.34	0.32	0.54	0.11	0.16	0.26	0.34	0.08	0.38	0.11	0.62	0.22
Kurtosis		1.37	0.25	1.68	0.21	0.65	1.93	0.53	2.22	1.31	0.68	8,09	4.71
Standard error	116.35	14.11	14.11	0.07	0.10	0.09	0.001	6.29	0.13	8.22	0.99	12.11	0.16
Coefficient of variation	15.74	3.93	3.93	24.32	5.62	5.90	4.82	5.87	4.96	9.01	9.80	7.28	7.97

Fluoride-containing waters are taken to a special pipe system, but they are not adequately managed. At the surface they join pre-treated wastewater from mines and are discharged together to the river. Thus, many valuable properties of these waters are lost.

Epidemiological tests show that in Lublin Voivodship and close-by districts of Poland, people have many dental and bone problems which comprise osteoporosis, osteopenia, parodontium, rheumatic arthropathy, etc. The results of many medical studies confirm good absorption of fluorides from water to human organism by mucous membrane in oral cavity and alimentary canal, and also by the skin [9]. Therefore, it would be possible to drink, rinse or take baths using fluoride waters from Jurassic formation of LCB. A similar procedure can be used in paradentosis and applied to patients after surgical operations and other curative procedures. Fluorides used from water accelerate bone remineralisation in osteoporosis and in early stage attenuate decrease of tooth enamel and make it more resistant. Method of therapy with fluoride waters is used in Poland for the treatment of patients in Cieplice Śląskie near Jelenia Góra (SW Poland). There are springs named "Marysieńka" containing fluorides in mineral water in the concentrations of about 10 mg F/dm^3. The results of therapies and research conducted by scientists from Medical Academy of Wrocław are interesting and significant.

CONCLUSION

Hydrogeological conditions of Lublin Coal basin were configured by many geological phenomena. Jurassic sediments contain waters with elevated quantity of fluorides. In the present study, various aspects have been outlined. Originally pure and rich in mineral compounds, Jurassic waters discharged to the river, loose their curative properties. Using them in water therapies would help many patients in health recovery or healthy people in preserving health. Waters used in balneological therapy or prophylaxes are non-invasive, effective and natural. Also protection of the environment can benefit from it. Fewer fluorides will get into the natural environment. As the results of water analyses show, Jurassic waters retain their chemical composition. The composition of ions, also hydogeological characteristics is stable in this formation. Chemical ingredients are independent on pumped-up mine water quantity.

Considering the insulation of Jurassic waters from the ground surface and seasonal changes, as well as only local disturbance to water flow, it is evident that each parameter confirms its stability. This is of a crucial importance as the basis for balneological treatment.

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