

## SELECTED PROCESSES IN ACIDULOUS WATERS FROM ŚWIERADÓW ZDRÓJ IN THE LIGHT OF THE RESULTS OF CHEMICAL ANALYSES OVER THE LAST THIRTY YEARS

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**Abstract:** In this paper the variability of chemical composition of Świeradów Zdrój acidulous waters for over thirty years is presented. Attempts were made at the interpretation of some noticeable effects occurring in these waters. Irregular fluctuations of free carbon dioxide content in acidulous waters (waters contained more than 1000 mg/dm<sup>3</sup> of free CO<sub>2</sub>) and the lack of a general trend in its changes, as well as slow and constant decrease of total dissolved solids (TDS) in shallow intakes should be underlined. TDS changes in time are the result of various stages of deep circulation waters mixing with slightly mineralized shallow waters. To a certain extent, these changes may depend on the chemical composition changes of deep circulation acidulous waters. Correlation of the TDS changes in time with the variability of some ions concentration (mainly HCO<sub>3</sub><sup>-</sup>, Ca<sup>2+</sup>, rarely Mg<sup>2+</sup>, K<sup>+</sup>) testifies to the origins of these ions from dissolution of rocks by acidulous waters of deep circulation. The origin of other ions should be connected with shallow circulation waters and with deep circulation acidulous waters as well. The lack of correlation between free carbon dioxide contents and concentration of hydrogen carbonate ion as well as lack of correlation between pH and CO<sub>2</sub> and HCO<sub>3</sub><sup>-</sup> concentration has not been explained yet and requires further research.

**Abstrakt:** W pracy przedstawiono zmienność składu chemicznego szczaw Świeradowa Zdroju na przestrzeni ostatnich trzydziestu kilku lat. Podjęto także próbę interpretacji niektórych z zaobserwowanych zjawisk zachodzących w tych wodach. Na szczególne podkreślenie zasługuje stwierdzenie nieregularnych wahań zawartości wolnego dwutlenku węgla w szczawach oraz brak generalnego trendu jej zmian, a także powolny, stały spadek mineralizacji ogólnej w płytkich ujęciach. Korelacja zmian mineralizacji ogólnej (TDS) w czasie ze zmiennością stężeń niektórych jonów świadczy o pochodzeniu tych jonów z rozpuszczania skał przez szczawy głębokiego krążenia. Brak korelacji pomiędzy zawartością wolnego dwutlenku węgla a stężeniem jonu wodorowęglanowego nie został wyjaśniony i wymaga dalszych badań.

**Key words:** Acidulous waters, total dissolved solids, CO<sub>2</sub>, Świeradów Zdrój, origin of ions, water mixing.

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### INTRODUCTION

Świeradów Zdrój is a spa, located in the Sudety Mountains (SW Poland), near the Czech and German borders. This area is located within the geological unit called Karkonosze–Izera block, which is a big structural unit belonging to western Sudety Mountains. It consists of two main parts – the granite massif of Karkonosze Mountains and its metamorphic covering layer. The spa surroundings are located within the metamorphic covering layer, which is built mainly of different kinds of gneisses, granite-gneisses and schists (Fig. 1). Insertions of vein rocks (aplites, quartz veins and amphibolites) amongst these main rock types also appear. The age of this rock formation is considered as late Precambrian. Due to the mountaineous type of this area, the above

mentioned rocks lie only under the thin cover of Quaternary bed and weathered clays, gravels and slope rubbles. Also the bottoms of river valleys are lined with Quaternary deposits (Fistek, 1967; Fistek *et al.*, 1975; Ciężkowski *et al.*, 1996).

Within the metamorphic rocks two dislocation directions, NW–SE and NE–SW, can be distinguished. The main fault of this area is the so-called spring fault of Świeradów Zdrój directed NW–SE, interrupted by lateral dislocations, running in NE–SW direction. The locations of these slits are considered as principal areas of curative waters circulation in the Karkonosze–Izera block (Fistek, 1967; Fistek *et al.*, 1975; Ciężkowski, 1983, 1990; Dowgiało *et al.*, 1969;

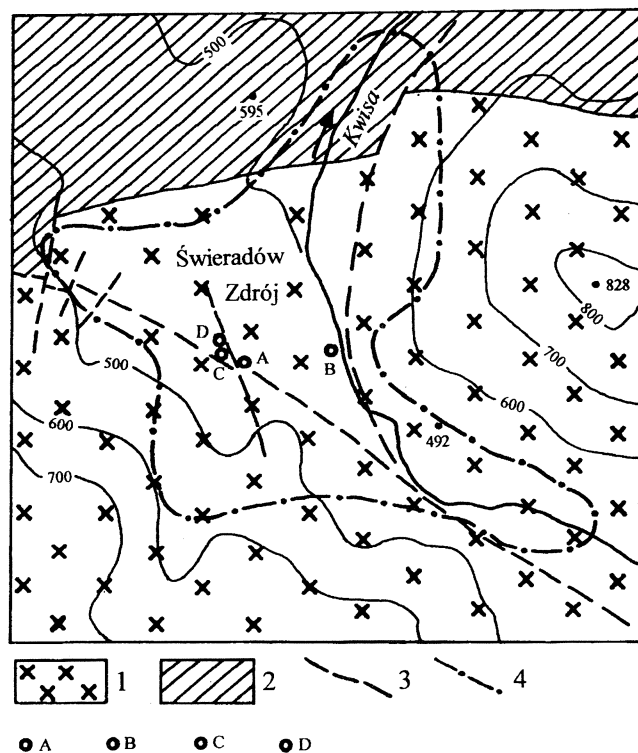


Fig. 1. Generalized geological sketch of Świeradów Zdrój neighbourhood (after Fistek, 1967; Szalamacha & Szalamacha, 1984). 1 – various types of gneisses and granite-gneisses, 2 – various types of metamorphic schists (mainly mica schists), 3 – faults, 4 – boundary of built-up area of Świeradów Zdrój. Intakes of mineral waters: A – Górne spring, B – Zofia spring, C – borehole 1A, D – borehole 2P

Fistek & Teisseyre, 1967; Szmytówna, 1958; Teisseyre, 1954; Teisseyre, 1966).

As curative waters from Świeradów Zdrój for balneological purposes two kinds of waters are exploited – slightly mineralized radon containing waters of shallow circulation and radon containing acidulous waters (waters contained more than  $1000 \text{ mg/dm}^3$  of free  $\text{CO}_2$ ). Their final physico-chemical character is created during the processes of mixing in different proportions of acidulous waters (with a chemical composition formed at low depths) with shallow slightly mineralized, radon containing waters (Ciężkowski, 1983, 1990; Ciężkowski *et al.*, 1996).

The acidulous waters described in this paper contain carbon dioxide of juvenile origin, related to the last activities of Tertiary magmatism. Such a point of view is confirmed by the results of carbon stable isotope composition of carbon dioxide (Dowgiało, 1978).

At present in Świeradów Zdrój acidulous waters from the Górne spring and the 1A borehole are exploited, whereas in the past such waters were exploited also from the 2P borehole and the Zofia spring. In these intakes acidulous waters of a general type  $\text{HCO}_3\text{-Ca-(Mg), Rn}$  (Table 1) flow out of gneisses and granite-gneisses. In the Górne intake they are captured by means of three wells (No. 1, 2 and 3) 6 to 10 m deep with a total discharge of  $0.5 \text{ m}^3/\text{h}$ , hydraulically connected together. The discharge of well No. 3 is higher than

Table 1

Hydrochemical types of water from selected intakes located in Świeradów Zdrój

Intake	Official hydrochemical types in the year of confirmation (year)	Recharge ( $Q[\text{m}^3/\text{h}]$ ) and temperature ( $t [^\circ\text{C}]$ ) in the year of confirmation	Hydrochemical type according to the latest analyses (year)
Górne 1	0.05% acidulous water slightly mineralized, Rn (1976)	$Q = 0.5$ $T = 10.0$	0.02% acidulous water $\text{HCO}_3$ , Fe, Si, Rn (1996)
Górne 2	0.05% acidulous water slightly mineralized, Rn (1976)		0.02% acidulous water $\text{HCO}_3\text{-Ca}$ , Si, Rn (1996)
Górne 3	0.05% acidulous water slightly mineralized, Rn (1976)		0.03% acidulous water $\text{HCO}_3$ , Si, Rn (1996)
Zofia	0.09% acidulous water $\text{HCO}_3\text{-Ca-Mg}$ , Rn (1970)	$Q = 0.2$ $T = 7.0$	0.09% acidulous water $\text{HCO}_3\text{-Ca}$ , Fe, F, Si, Rn (1979)
1A	0.1% acidulous water slightly mineralized, Fe, Rn (1989)	$Q = 0.7$ $T = 8.6$	0.08% acidulous water $\text{HCO}_3\text{-Mg}$ , Fe, F, Si, Rn (1996)
2P	0.2% acidulous water $\text{HCO}_3\text{-Ca-Mg}$ , Fe (1970)	$Q = 0.24$ $T = 9.0$	0.27% acidulous water $\text{HCO}_3$ , Fe, F, Si (1995)

the total discharge of wells No. 1 and No. 2 combined. The discharges of wells No. 1 and No. 2 are similar. In the 1A borehole (discharge  $0.7 \text{ m}^3/\text{h}$ ) acidulous waters are taken from a depth of 34 - 53 m. Yet at present non exploited intakes – the Zofia spring and the 2P borehole acidulous waters were taken from 8.5 m with a discharge of  $0.2 \text{ m}^3/\text{h}$  and from 155–160 m, 185–218 m, 250–265 with a discharge of  $0.24 \text{ m}^3/\text{h}$ . Exploitation was performed or is being performed on self-acting basis in all mentioned intakes.

## METHOD OF INVESTIGATION

In the intakes mentioned above (Górne, Zofia, 1A and 2P) regular chemical analyses of curative waters, have been carried out yearly by the balneological laboratory of BPI-UTBU "Balneoprojekt" in Szczawno Zdrój. This allows us to draw conclusions related to hydrochemical changes and their character, taking place for over thirty years in the acidulous waters flow system within Karkonosze-Izera block in the Świeradów Zdrój area. It enabled the authors to create a hydrochemical data base for acidulous waters of this region and to create statistical calculations by means of the EXCEL computer programme.

Statistical analysis was carried out for the significance level  $\alpha = 0.05$ , with the amount of analyzed data for particular components from 8 to 36. For the interpretation, coeffi-

Table 2

Percentage content of common waters in curative water intakes in Świeradów Zdrój on the base of  $\text{HCO}_3^-$  ion (after Cieżkowski *et al.*, 1996)

Intakes	Analyzed period	Number of analyses	TDS in water [ $\text{mg}/\text{dm}^3$ ]		Percentage contents of common waters in particular intakes (in whole analyzed period)
			max.	min.	
Górne 1	1969–1989	22	471	187	82–95
Górne 2	1969–1996	22	450	154	83–96
Górne 3	1875–1996	38	631	295	77–92
Zofia	1944–1979	20	1049	851	61–68
1A	1975–1996	25	865	574	68–79
2P	1972 and 1986–1995	11	2695	1422	0–47

coefficients of linear correlation (R) higher than the critical value for the chosen significant level were taken into account. As a high correlation the value of  $R \geq 0.70$  was taken.

## RESULTS AND DISCUSSION

For over thirty years no common trend in the variability of chemical parameters of waters of all the researched intakes has been observed. It is caused by the different depth of intakes, which determines that in outflowing acidulous radon containing water, common radon waters diluting acidulous water of deep circulation, create a different percentage of outflowing mixture. The bigger admixture of common waters contain shallow acidulous waters intakes – Górne and in smaller amounts – Zofia and 1A, whereas the deepest 2P intake contains the lowest amount of common waters of shallow circulation. It is showed in Table 2. For all intakes a low correlation (correlation coefficient below critical value for customary significant level) was observed. Also essential and even high negative correlation between radon content and total dissolved solids (TDS) was noticed, confirming the origin of radon from shallow circulation waters (Table 3) (Cieżkowski, 1983, 1990; Przylibski & Żebrowski, 1996).

In connection with the statements mentioned above, the interpretation of hydrochemical data was held for two groups of intakes – shallow springs (Górne and Zofia) and boreholes (1A and 2P), whereas in some cases the chemical composition of water from Zofia spring was more similar to the chemical composition of acidulous waters from borehole of lower depth (1A) rather than from Górne spring (Table 3).

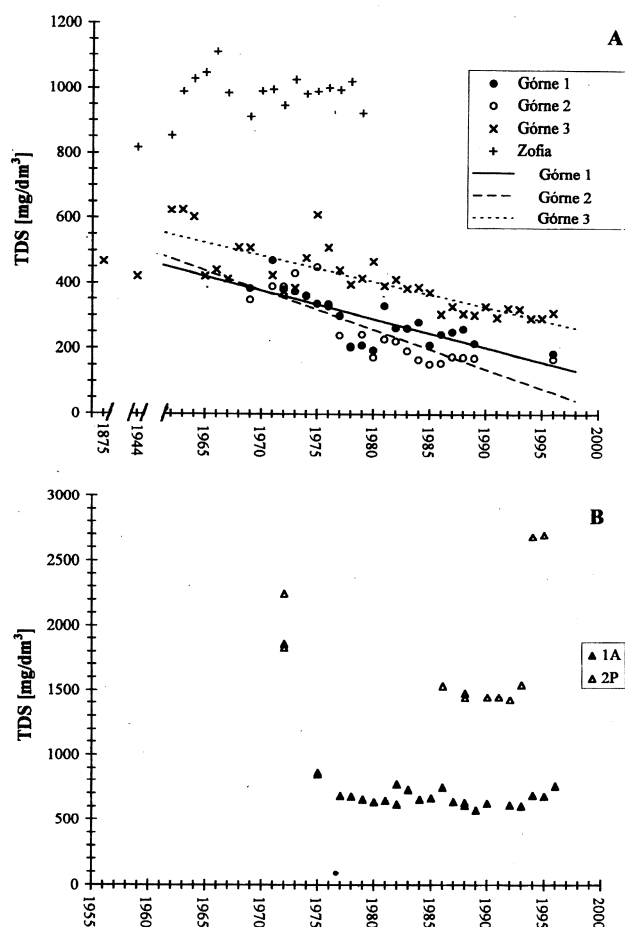


Fig. 2. Variability of TDS in springs (A) and boreholes (B) of Świeradów Zdrój acidulous waters in time. Lines represent trend of TDS changes in time in waters from particular intakes

For over thirty years chemical compounds fluctuations were observed in all intakes (Table 2, Fig. 2) reflecting quantitative changes in the process of mixing of deep and shallow common waters. In the acidulous waters of intakes Zofia and 1A the fluctuations of TDS level in time were noticed, however without visible trend (Fig. 2). Acidulous waters taken from particular wells of Górne spring show different types of fluctuations. All they show a clear decreasing tendency of TDS in time, which can be described by the following equations:

$$\text{the Górne intake No. 1: } y = -8.73x + 457.33 \quad (1)$$

$$\text{the Górne intake No. 2: } y = -12.04x + 488.01 \quad (2)$$

$$\text{the Górne intake No. 3: } y = -7.90x + 558.03 \quad (3)$$

where:

$x$  – ordinal number of the year, beginning from the date of first analysis [–],

$y$  – value of TDS [ $\text{mg}/\text{dm}^3$ ].

The obtained equations were calculated based on data between 1970 and 1996, 1970 and 1996, 1962 and 1996 years respectively (Fig. 2A).

The character of TDS changes of acidulous waters taken from the 2P borehole is different than from the oth-

Table 3

Results of the latest chemical analyses of Świeradów Zdrój selected intakes. Components and physico-chemical properties represent essential (lighter shade) and high (darker shade, correlation coefficient over 0.7) correlation with TDS of water during the whole analyzed period. Symbol (-) means negative correlation

Intake	Górne 1	Górne 2	Górne 3	Zofia	1A	2P
date	27.02.1996	27.02.1996	27.02.1996	11.05.1979	27.02.1996	02.02.1995
temperature	10.8	11.8	10.5	7.2	8.1	7.3
pH	4.83	4.84	5.22	6.09	5.58	6.42
Na <sup>+</sup>	8.5	7.1	12.0	37.5	27.7	51.0
K <sup>+</sup>	3.0	4.0	5.3	5.8	11.5	22.8
Li <sup>+</sup>	0.0	0.0	0.0	0.2	0.1	(-) 0.2
NH <sub>4</sub> <sup>+</sup>	0.2	0.08	0.2	0.1	0.2	0.2
Ca <sup>2+</sup>	12.5	18.1	29.4	100.15	51.3	137.4
Mg <sup>2+</sup>	7.3	6.0	16.5	42.89	47.6	83.4
Fe <sup>2+</sup>	12.0	4.2	4.9	15.6	25.6	422.0
Mn <sup>2+</sup>	0.05	0.05	0.07	0.38	0.1	0.3
F <sup>-</sup>	(-) 0.4	0.2	0.7	2.1	2.0	1.4
Cl <sup>-</sup>	12.4	(-) 10.6	(-) 8.8	9.55	8.8	35.5
SO <sub>4</sub> <sup>2-</sup>	19.3	21.0	20.4	14.4	6.0	6.5
HCO <sub>3</sub> <sup>-</sup>	82.4	70.2	183.2	624.7	518.0	1868.8
NO <sub>3</sub> <sup>-</sup>	0.13	4.6	2.0	0.1	0.5	0.35
H <sub>2</sub> SiO <sub>3</sub>	28.6	23.4	28.6	72.8	(-) 57.2	65.0
<b>TDS</b>	<b>186.78</b>	<b>169.48</b>	<b>312.07</b>	<b>926.17</b>	<b>756.5</b>	<b>2694.85</b>
<b>CO<sub>2</sub></b>	<b>1764</b>	<b>1470</b>	<b>1827</b>	<b>(-) 2838</b>	<b>2492</b>	<b>(-) 2450</b>
Rn	10.9	3.3	(-) 17.1	(-) 8.0	(-) 2.1	0.4

ers. They can be described by small fluctuations during the period of 1986–1993, and then strong TDS increase by almost 75% (from 1538 mg/dm<sup>3</sup> to 2679 mg/dm<sup>3</sup>) (Fig. 2B).

In connection with high noticed TDS fluctuations of acidulous waters from Świeradów Zdrój also the variability of particular ions content by correlation of their concentrations with TDS was examined. The TDS of acidulous waters flowing out in this spa is controlled by the TDS of deep circulation acidulous waters, later being diluted by slightly mineralized waters. Significant correlations can be the indicator of the origin of a given ion. This origin is related to the dissolution of rocks located in the zone of deep circulation of acidulous waters, which represent different kinds of metamorphic schists (Cieżykowski, 1983).

In the case of Zofia and 2P intakes the small amount of data makes the statistical analysis highly uncertain.

High correlation with TDS is shown by HCO<sub>3</sub><sup>-</sup> and Ca<sup>2+</sup> ions while high or essential correlation for all intakes is shown by Mg<sup>2+</sup> and K<sup>+</sup> ions (Table 3). It comes from the statement that linear increase of these ions content with the increase of TDS prove that their origin is connected with

acidulous waters of deep circulation. A very high correlation (correlation coefficient about 0.95–0.99) between HCO<sub>3</sub><sup>-</sup> ion and TDS, with the exception of well No. 1 from Górne intake (R = 0.88), was noticed. An essential and, occasionally, high correlation with TDS was noticed for Na<sup>+</sup>, Fe<sup>2+</sup>, Mn<sup>2+</sup> ions, although not in all intakes. It tells us about the origin of these ions from acidulous water of deep circulation, and, at the lower scale, from common shallow waters (Table 3).

The other ions (Li<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, F<sup>-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup>) do not show an essential correlation in all intakes, which can be explained by their origin, connected with deep circulation waters (acidulous waters) as well as with shallow circulation waters. An analogous conclusion is drawn also for meta-silicic acid (Table 3). "Double" origin of these compounds can be explained by more intensive activity of weathering processes in the case of shallow circulation waters, and by longer reaction time between water and rock in case of deep circulation waters. These conclusions are confirmed by the results of chemical analyses of shallow circulation radon waters. According to them, the contents of the compounds

mentioned above make about half of their content in the analyzed acidulous waters.

Changes of chemical composition of Świeradów Zdrój acidulous waters in time may be observed by comparing their hydrochemical types following analyses over several decades (at the moment of exploitation resources confirmation) with the latest results (Table 1).

In the researched acidulous waters two gas components also occur. Radon as a radioactive component of shallow slightly mineralized waters will be the subject of separate papers. Yet carbon dioxide is the essential component, which creates the character of Świeradów Zdrój acidulous waters. Contrary to TDS, changes of free carbon dioxide amount in researched acidulous waters have the capacity of irregular fluctuations, showing no general trend. It tells us of its independent inflow from deeper parts of the earth's crust. The deep fall of its contents in all exploited intakes in 1980 is a characteristic phenomenon (Fig. 3). Character of irregular fluctuations of free carbon dioxide contents is underlined by lack of correlation or low values of correlation (sometimes negative) between  $\text{CO}_2$  contents and TDS in all intakes (Table 3).

Nowadays the juvenile origin of this gas in Sudety Mts. acidulous waters is accepted. The isotopic composition of carbon advocates it. In spite of the fact that the isotopic balance between  $\text{CO}_2$  and  $\text{HCO}_3^-$  in Sudety Mts. acidulous waters is rarely observed, deviations of  $\delta^{13}\text{C}$  differences from differences typical for conditions of isotopic balance are relatively small. Because of this, in many cases, it is considered that  $\text{HCO}_3^-$  ion came into existence as a result of the reaction between carbon dioxide and minerals of crystalline rocks (Dowgiatło, 1978). The presence of  $\text{HCO}_3^-$  ion being a result of reaction between carbon dioxide and rock, controlling simultaneously concentrations of this ion in acidulous water, is contradictory to lack of observed high positive correlation between  $\text{CO}_2$  and  $\text{HCO}_3^-$  ion. Carbon dioxide enabling dissolution and maintenance of  $\text{HCO}_3^-$  ion in the solution (acidulous water), being substrate and "catalyst" of this reaction, which product is  $\text{HCO}_3^-$  ion should be strongly correlated. Another factor which controls equilibrium between concentrations of  $\text{CO}_2$  ( $\text{H}_2\text{CO}_3$ ) and  $\text{HCO}_3^-$  in the solution is pH. However, in this case the influence of pH values changes on concentration changes of  $\text{CO}_2$  ( $\text{H}_2\text{CO}_3$ ) and  $\text{HCO}_3^-$  was not observed. Correlation coefficients between pH and  $\text{HCO}_3^-$  ion concentration and between pH and  $\text{CO}_2$  ( $\text{H}_2\text{CO}_3$ ) content in the solution are lower than boundaries confirming the presence of dependence between these parameters. In the present state of knowledge explaining these phenomena is not possible and demands further research.

## CONCLUSIONS

Strong fluctuations of TDS in time in acidulous waters of Świeradów Zdrój can be observed. The noticed decrease of TDS in all wells of the Górne intake should be underlined. Yet the fluctuations of free carbon dioxide contents, which creates the character of acidulous waters, are irregular and show no general trend.

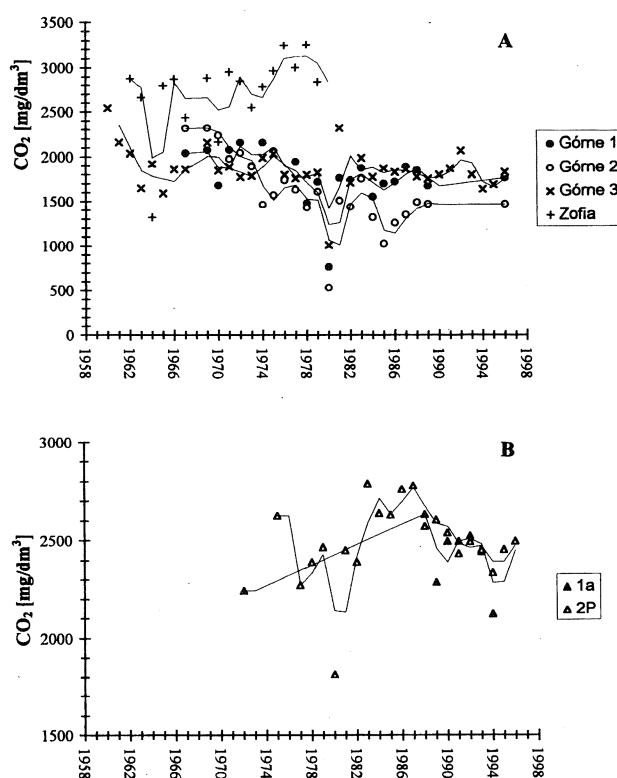


Fig. 3. Variability of  $\text{CO}_2$  content in springs (A) and boreholes (B) of Świeradów Zdrój acidulous waters in time. Continuous lines represent running averages of  $\text{CO}_2$  contents in waters from particular intakes

Fluctuations of chemical composition and TDS changes in acidulous waters of Świeradów Zdrój are the result of the different level of dilution of deep circulation acidulous waters by shallow slightly mineralized waters. At a lower scale they may come from a fact of chemical composition changes of deep acidulous waters. The influence of mixing on TDS changes is confirmed by the lack of correlation (or negative correlation) of radon concentration with TDS.

Because of stating the fact of high correlation of some ions (mainly  $\text{HCO}_3^-$  and  $\text{Ca}^{2+}$ , rarely  $\text{Mg}^{2+}$  and  $\text{K}^+$ ) with TDS in all intakes, their presence in acidulous waters should be connected with deep circulation waters. Essential or high correlation with TDS was noticed for  $\text{Na}^+$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$  ions, whereas it was not observed in all intakes, which attest the origin of these ions mainly from deep circulation acidulous waters, and, at a lower scale, from shallow common waters. The other ions ( $\text{Li}^+$ ,  $\text{NH}_4^+$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ ) and metasilicic acid do not show essential correlation in all intakes, which should be explained by their origin, connected with deep circulation waters (acidulous waters) as well as with shallow waters.

The presence of  $\text{HCO}_3^-$  ion, being a result of reaction between carbon dioxide and rock, controlling simultaneously concentrations of this ion in acidulous water, is contradictory to the lack of observed high positive correlation between  $\text{CO}_2$  and  $\text{HCO}_3^-$  ion. Also the influence of pH changes on the content of these components in solution were

not observed. Explaining this phenomenon demands further research.

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#### Streszczenie

### WYBRANE PROCESY W SZCZAWACH ŚWIERADOWA ZDROJU W ŚWIETLE WYNIKÓW ANALIZ CHEMICZNYCH Z OSTATNICH TRZYDZIESTU LAT

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W pracy przedstawiono wybrane procesy zmian chemizmu szczaw Świeradowa Zdroju na podstawie obserwacji z ostatnich trzydziestu kilku lat. Omawiane wody występują w obrębie bloku karkonosko-izerskiego (Fig. 1). Wykorzystywane są do celów balneologicznych i reprezentowane przez dwa zasadnicze typy: słabo zmineralizowane wody radoczynne płytkiego krążenia oraz szczawy radoczynne. Obecnie eksploatowane ujęcia Górne i 1A oraz niewykorzystywane już 2P i Zofia ujmują szczawy o generalnym typie  $\text{HCO}_3\text{-Ca-Mg}$ , Rn (Tabela 1). Szczawy te zawierają dwutlenek węgla pochodzenia juwenilnego, związany z ostatnimi przejawami trzeciorzędowego magmatyzmu. Pogląd taki potwierdzają badania składu izotopowego węgla w dwutlenku węgla.

W omawianych szczawach rozcieńczające je zwykle wody radoczynne stanowią różny procent wypływającej mieszaniny. Większą domieszkę wód zwykłych zawierają płytkie ujęcia szczaw: Górne, Zofia oraz 1A (Tabela 2).

W związku z powyższym interpretację danych hydrochemicznych przeprowadzono dla dwóch grup ujęć – płytkich źródeł (Górne i Zofia) oraz odwiertów (1A i 2P), przy czym w niektórych wypadkach skład chemiczny szczaw z ujęcia Zofia bardziej zbliżony był do składu szczaw z płytszego z odwiertów (1A) niż z ujęcia Górne (Tabela 3).

W ciągu ostatnich trzydziestu kilku lat zaobserwowano we wszystkich ujęciach wahania składu chemicznego wpływających szczaw, co jest odzwierciedleniem zmian ilościowych w procesie mieszania się ich z płytkimi wodami zwykłymi (Tabela 2). W szczawach ujęć Zofia i 1A notowane były wahania poziomu mineralizacji ogólnej (TDS) w czasie, jednakże nie wykazujące żadnego wyraźnego trendu. Odmienne zachowują się natomiast szczawy ujęte w poszczególnych studniach źródła Górne. Wszystkie one wykazują wyraźną tendencję spadkową TDS w czasie. W odwiercie 2P występują niewielkie wahania w latach 1986–1993, a następnie gwałtowny wzrost mineralizacji o blisko 75% (od  $1538 \text{ mg/dm}^3$  do  $2679 \text{ mg/dm}^3$ ) (Fig. 2).

Wysoką korelację z TDS wykazują jony  $\text{HCO}_3^-$  i  $\text{Ca}^{2+}$ , natomiast wysoką lub istotną jony  $\text{Mg}^{2+}$  i  $\text{K}^+$  dla wszystkich ujęć (Tabela 3). Wynika z tego, że notowany jest liniowy wzrost zawartości tych jonów wraz ze wzrostem mineralizacji, czyli ich geneza związana jest ze szczawami głębokiego krążenia. Istotna, a rzadziej wysoka korelacja z TDS zanotowana została dla jonów  $\text{Na}^+$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ , przy czym nie była ona obserwowana we wszystkich ujęciach. Świadczy to o pochodzeniu tych jonów ze szczaw głębokiego krążenia, a w mniejszym stopniu ze zwykłych wód płytkiego krążenia (Tabela 3).

Pozostałe jony ( $\text{Li}^+$ ,  $\text{NH}_4^+$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  i  $\text{NO}_3^-$ ) nie wykazują istotnych korelacji we wszystkich ujęciach, co należy tłumaczyć ich genezą, związaną zarówno z wodami głębokiego krążenia (szczawami), jak i z wodami płytkimi. Analogiczny wniosek wyciągnięto także dla kwasu metakrzemowego (Tabela 3).

W przeciwieństwie do TDS, zmiany ilości wolnego dwutlenku węgla w badanych szczawach mają charakter nieregularnych wahań, nie wykazujących żadnego generalnego trendu (Fig. 3). Świadczy to o jego niezależnym dopływie z głębszych partii skorupy ziemskiej.

Obecność jonu wodorowęglanowego będącego wynikiem reakcji dwutlenku węgla ze skałą, kontrolującego jednocześnie stężenia tego jonu w szczawie stoi w sprzeczności z brakiem obserwowanej korelacji lub jej niskimi wartościami pomiędzy zawartością  $\text{CO}_2$  i jonu  $\text{HCO}_3^-$ . Dwutlenek węgla umożliwiającą rozpuszczanie i utrzymywanie się jonu wodorowęglanowego w

roztworze (szczawie), będący substratem i "katalizatorem" tej reakcji, której produktem jest jon  $\text{HCO}_3^-$ , powinny być silnie skorelowane ze sobą. W obecnym stanie wiedzy wytłumaczenie tego zjawiska nie jest możliwe i wymaga prowadzenia dalszych badań.

