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STATISTICAL ANALYSIS OF TWO IMPORTANT CHEMICAL FEATURES (TDS AND (HCO_3^-) CONTENT) IN SUDETIC THERAPEUTIC WATERS

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Abstract: Two important chemical features of therapeutic waters from 57 intakes in 13 Sudetic health resorts, i.e. total dissolved solids (TDS) and bicarbonate ion (HCO_3^-) content, tested with the Kolmogorov test at the significance level α=0.05, during the whole exploitation period, reveal normal distributions. It bears evidence of little variability of these features. Intervals of the most frequent (normal) [HCO_3^-] content values in individual intakes, determined using the three standard deviations method (3σ) are in most cases concordant with real values. These intervals can be used for verification of monitoring measurements (elimination of incorrect determinations) and/or can indicate sudden changes of chemical composition of exploited therapeutic waters.

Abstrakt: Dwie podstawowe własności wód leczniczych w 57 ujęciach z 13 miejscowości uzdrowiskowych Sudetów: suma substancji rozpuszczonych (TDS) i zawartość jonu wodorowęglanowego (HCO_3^-), przetestowane testem Kołmogorowa na poziomie istotności α=0.05 na przestrzeni całego okresu eksploatacji, wykazują rozkłady normalne, co świadczy o ich dużej stałości. Wyznaczone metodą trzech odchyleń standardowych (3σ) przedziały wartości najczęściej występujących dla zawartości (HCO_3^-) w poszczególnych ujęciach pokrywają się zwykle z wartościami rzeczywistymi.

Uzyskane przedziały normalnych zawartości anionu wodorowęglanowego mogą być wykorzystywane do weryfikacji prowadzonych obserwacji stacjonarnych (eliminowanie błędnych oznaczeń) i/lub sygnalizacji gwałtownych zmian składu chemicznego eksploatowanej wody leczniczej.

Key words: chemical composition changes, therapeutic waters, Sudetes, statistical analysis.

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INTRODUCTION

According to the Polish geological and mining law, exploitation of therapeutic waters requires also protection of its deposits, by means a.o. of a monitoring system. The chemical composition of water, including TDS (calculated as the sum of all of anions and cations indicated in therapeutic water), is part of this system. Once a year a control analysis is carried out for health resorts mainly by laboratories of such institutions like 'Balneoprojekt' Health Resorts Design and Technical Service Bureau or Department of Drilling, Petroleum and Gas of the Academy of Mining and Metallurgy in Kraków. Besides, health resorts perform, with various frequency, their own measurements of the principal features of therapeutic waters, including indicator determinations. Since carbonated waters rich in CO_2 are the most common ones, bicarbonate ion (HCO_3^-) is most often used as an indicator parameter.

The [HCO_3^-] concentration is an important indicator of environmental changes in the quality of the water exploited. On the basis of rich archival material from the observation period, exceeding 30 years for most intakes, and in some cases even 100 years (e.g. 'Emilia' intake in Długopole Zdrój or five intakes in Cieplice Śląskie Zdrój), the author determined intervals of the indicator's normal (most common) values and compared them with real values observed.

GEOLOGICAL BACKGROUND

Sudetes are an area, where in 13 resorts occur waters declared as therapeutic (at Gorzanów till 1984 only) (Ciężkowski, 1990). In most cases there are carbonated waters; in several sites occur thermal waters, radioactive waters and sulphurous waters (Fig. 1).

Fig. 1 shows the occurrence of these waters on the schematic geological map of the Sudetes (after Oberc, 1952; Geological Map of Lower Silesia, 1995). The Sudetes' bedrock are igneous and metamorphic rocks, which exhibit common directly on the ground-surface. It concerns specially granitic massifs (Karkonosze massif, Strzegom–Sobótka massif, Strzelin massif, Kłodzko–Złoty Stok massif

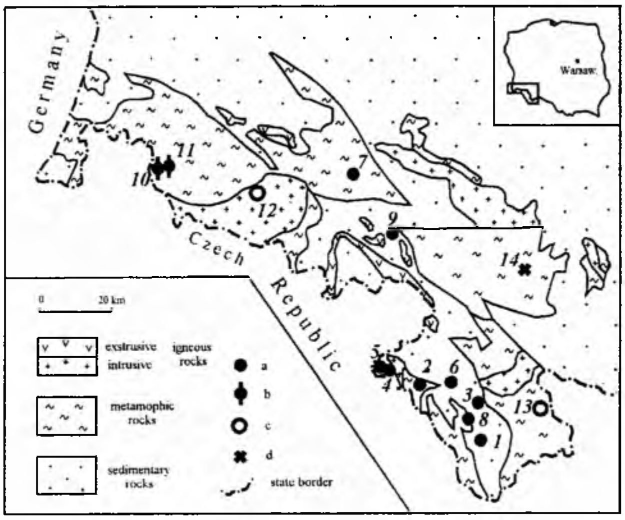

Fig. 1. The occurrence of selected Sudetic mineral waters on the background of generalized geological setting (after Oberc, 1952; Ciężkowski, 1990; Geological Map of Lower Silesia, 1995). a – carbonated waters: 1 – Długopole Zdrój, 2 – Duszniki Zdrój, 3 – Gorzanów, 4 – Jeleniów, 5 – Kudowa Zdrój, 6 – Polanica Zdrój, 7 – Stare Rochowice, 8 – Szczawina, 9 – Szczawno Zdrój; b – radon-bearing carbonated waters: 10 – Czerniawa Zdrój, 11 – Świeradów Zdrój; c – thermal waters: 12 – Cieplice Zdrój, 13 – Lądek Zdrój; d – sulphurous waters: 14 – Przerzeczyn Zdrój

and Kudowa massif) and metamorphic zones (Izerskie Mts., Kaczawskie Mts., Sowie Mts., Bystrzyckie and Orlickie Mts., Śnieżnik massif, Kłodzko metamorphic zone and Niemcza zone), where the predominant rocks are mica shists, gneisses, phyllites and greenstones. The relationship between geological setting, tectonics and formation of chemical composition of the Sudetic mineral waters was presented in detail in e.g.: Dowgiałło (1976), Fistek (1977), Ciężkowski (1980, 1990).

The most common Sudetic mineral waters are carbonated waters, which occur almost in all hydrogeological units and lithological types of rocks. Their occurence is associated with deep dislocation zones, which form migration pathways for CO_2 of deep origin. With deep faults in granites of the Karkonosze massif and in metamorphic rocks (mica shists, gneisses) of the Śnieżnik massif is associated the occurence of thermal waters also. Radioactive waters are common in the sites, where igneous or metamorphic rocks appear on the ground-surface and/or zones strongly influenced by tectonics occur (Przylibski, 1997).

METHOD OF INVESTIGATION

In order to maintain the highest possible homogeneity of the initial material the author used only archival annual control analyses owned by individual health resorts and partly published (Jarocka, 1976). Selection of data resulted in rejection of results obtained, e.g.: during drilling rendering the deposit accessible (e.g. intake 'no 18' in Kudowa Zdrój – all available analyses, or intake 'P-300' in Polanica Zdrój from 27.07.1966 to 23.04.1967), or from periods when exploitation took place in technical conditions different from today's (e.g. the 'Studzienne' intake in Szczawno Zdrój – analyses from the years 1937, 1954 and 1963, or the 'Jan' intake in Czerniawa Zdrój – analyses from 1928 and 1933) (Jarocka, 1976).

In the statistical analysis results of determinations being part of the monitoring system have not been taken into consideration. Firstly, because monitoring is not being carried out in all of health resorts. Secondly, it is difficult to evaluate the accuracy of these measurements; there are no publications touching this problem.

Apart from therapeutic waters (mineral ones and/or containing specific components and/or of temperature exceeding 20 °C) also waters present in health resort areas which were not declared as therapeutic (in most cases slightly mineralized common waters) are considered in the paper (Table 1). They present the hydrochemical background for therapeutic waters.

Random samples obtained (Table 1 lists TDS and [HCO_3^-] data from particular intakes) were tested using the Kolmogorov goodness-of-fit test, where two hypotheses were put forward (Davis, 1986):

– H_0 : assuming concordance of distributions of the general population, from which the random samples originate, with the normal distribution,

– H_1 : opposite to H_0.

All tests were done for the significance level α=0.05.

The most popular goodness-of-fit test, also in hydrochemical investigations, is the chi-square test (χ^2) (e.g. Roszak, 1987). In the present paper, the Kolmogorov test was applied for two reasons. Firstly, it can be used for testing samples with the size $n \geq 8$, and not $n \geq 30$ as in the χ^2 test. Secondly, the χ^2 test is not powerful and it is strongly dependent on a small number of degrees of freedom (Lusznie-wicz & Słaby, 1996) (i.e. small number of class intervals in the sample). The Kolmogorov test, on the other hand, may be used for samples not classified into intervals (Davis, 1986). Thus, a decision on acceptance or rejection of the null hypothesis at the same α significance level is more powerful in the case of the Kolmogorov test.

RESULTS OF INVESTIGATION

TESTING OF NORMALITY

Testing of the TDS distribution concordance with the normal distribution was carried out for 57 intakes from 13 localities ($n \geq 8$) (Table 1). The results indicate that there is no reason for rejection of the H_0 at the significance level accepted, which means that distributions of this features in the Sudetic therapeutic waters have a normal character. In spite of the fact that in several tens of intakes analysed, various chemical water types occur, with a different TDS value, exploited from various depths and in different hydrogeological conditions and with a different fraction of fresh waters of shallow circulation (calculated using the chemical data; Ciężkowski *et al.*, 1996) no explicit influence of each of these factors on the TDS distribution is observed. Normal distribution of TDS is also typical of shallow, common wa-

Table 1

Basic statistical parameters and $[HCO_3^-]$ values – real and determined using the 3σ method

Ordinal number of health resort	Intake name 1)	Sample size	Arithmetic average $\bar{x}$	Standard deviation σ	Skewness A_x	Real values of HCO_3^- concentrations		Normal values of HCO_3^- concentration (–3σ, +3σ) 3)	
						min	max.	min.	max
			mg/dm^3			mg/dm^3			
1	**Długopole Zdrój**								
	Emilia	35	677.2	156.7	+1.06	441.2	1037.0	207.2	1147.2
	Kazimierz	31	636.4	112.4	+1.84	483.5	972.7	299.2	973.6
	Renata	36	881.6	54.1	–1.49	671.2	983.0	719.2	1043.9
2	**Duszniki Zdrój**								
	Jan Kazimierz	34	981.9	142.1	–0.19	701.7	1204.0	555.5	1408.3
	Pieniawa Chopina	34	1505.4	105.1	+2.99	1346.0	1993.0	1190.1	1820.7
	Agata	21	1664.7	313.2	–	1050.0	2044.1	725.0	2604.4
	B-4	24	1793.0	75.4	–	1620.0	1952.0	1566.9	2019.1
	B-1	14	1709.8	281.4	–	1234.6	1998.3	865.5	2554.0
	Zimny Zdrój	7	597.0	49.3	–	527.1	671.2	–	–
	B-2	11	837.7	267.8	–	414.9	1263.1	34.4	1641.0
	B-3	30	1309.9	239.3	–0.71	571.2	1760.5	591.9	2027.8
3	**Gorzanów**								
	No 1 (Kaczka)	9	268.2	6.9	–	261.0	282.0	247.5	288.9
	No 2	6	497.5	13.8	–	482.6	518.6	–	–
	No 5 (upper level)	14	679.0	262.5	–	370.7	1214.0	0	1466.6
	No 6	17	745.5	87.8	–	535.6	873.4	482.1	1009.0
	No 5 (lower level)	19	1102.0	35.8	–	1049.0	1186.0	994.8	1209.3
4	**Jeleniów**								
	No 5	4	116.6	13.4	–	104.6	135.3	–	–
	No 8	4	218.6	27.9	–	188.0	254.2	–	–
	No 2	4	239.1	12.1	–	226.0	254.1	–	–
	J-150	45	828.6	155.1	+2.54	517.0	1586.5	363.2	1294.0
	Sarenka	11	1381.3	441.9	–	335.5	1772.0	55.8	2706.9
	P5	15	1572.9	120.1	–	1221.0	1727.4	1212.6	1933.2
5	**Kudowa Zdrój**								
	P1	23	340.2	16.8	–	286.2	365.7	289.7	390.7
	No 3 (Nowy Marchlewski)	44	1056.0	175.7	–0.60	695.5	1311.0	528.9	1583.0
	P4	23	1206.2	167.8	–	942.0	1579.0	702.6	1709.7
	Górne	10	1571.1	105.9	–	1370.0	1729.0	1253.3	1888.9
	No 26	4	1951.4	88.4	–	1859.0	2062.0	–	–
	No 2 (Moniuszko)	46	2187.1	86.7	–0.68	1952.0	2301.0	1926.9	2447.2
	K-200	37	2169.1	29.8	–0.78	2078.0	2226.0	2080.0	2258.4
	P6	22	3559.5	160.1	–	3363.6	3990.0	3079.2	4039.8
6	**Polanica Zdrój**								
	Pieniawa Józefa 2	15	609.3	39.4	–	545.2	660.9	491.0	727.6
	Pieniawa Józefa 1	32	797.6	140.2	+1.14	640.0	1246.0	377.1	1218.1
	Józef Stary	5	818.4	40.5	–	779.0	885.0	–	–
	Żelaziste	7	1158.7	74.6	–	1061.4	1266.0	–	–
	Wielka Pieniawa	37	1197.7	65.1	+1.79	1101.4	1419.0	1002.3	1393.1
	P-300	26	1908.0	212.1	–	1728.9	2017.8	1271.7	2544.4
7	**Stare Rochowice**								
	No 5	9	413.7	39.8	–	341.0	457.6	294.3	533.1
	No 6	7	1499.2	471.6	–	1006.8	2150.9	–	–
	No 2	6	2184.4	20.2	–	2151.8	2197.3	–	–
	No 1	9	2245.8	321.3	–	1769.5	2616.0	1281.9	3209.8

1) – names of intakes where water is not regarded at present as therapeutic are written in italics, 2) – calculated for samples with size n≥30, 3) – calculated for samples with size n≥8. Ordinal numbers of health resorts as in Fig. 1

Table 1 (continuation)

Ordinal number of health resort	Intake name[1]	Sample size	Arithmetic average $\bar{x}$	Standard deviation σ	Skewness A_x	Real values of HCO_3^- concentrations		Normal values of HCO_3^- concentration $(-3\sigma, +3\sigma)$[3]	
						min	max.	min.	max
			mg/dm^3			mg/dm^3			
8	Szczawina								
	Studzienne	17	452.6	22.9	–	387.3	490.5	383.9	521.3
	Szczawina-1	8	671.2	333.2	–	343.9	1418.9	0	1670.7
9	**Szczawno Zdrój**								
	No 14	5	277.4	10.1	–	268.0	293.0	–	–
	Mieszko-14	9	433.5	183.0	–	269.0	701.1	0	982.4
	Dąbrówka	41	1384.9	306.6	+0.06	808.5	1980.6	465.0	2304.7
	Młynarz	31	1466.9	233.2	+0.95	1079.0	2240.0	767.3	2166.5
	Marta	31	1569.6	278.5	+0.98	1118.0	2504.0	734.1	2405.2
	Mieszko	38	1920.5	277.9	+0.78	1398.7	2665.0	1086.8	2754.3
10	**Czerniawa Zdrój**								
	Radoczynne 1	12	7.0	5.1	–	0	18.4	0	22.3
	Radoczynne 2	9	7.2	4.4	–	3.7	18.1	0	20.4
	No 1	25	94.3	15.1	–	27.7	114.3	49.0	139.6
	Maria	10	493.0	153.9	–	364.9	861.8	31.4	954.6
	Jan	24	717.6	209.3	–	424.1	1458.0	89.6	1345.6
	No 4	27	2099.7	136.0	–	1922.0	2447.7	1691.6	2507.7
11	**Świeradów Zdrój**								
	Górne 1	21	145.9	49.1	–	79.7	245.0	0	293.3
	Górne 2	21	115.4	72.1	–	42.9	228.8	0	331.7
	Górne 3	37	251.8	72.1	+0.90	159.1	427.1	35.4	468.1
	1A	24	465.1	75.2	–	388.0	618.2	239.3	690.8
	Zofia	20	680.1	42.0	–	587.3	762.7	554.1	806.1
	2P	11	1307.5	353.2	–	999.0	1872.7	248.0	2367.0
	Radoczynne Zbiorcze	13	925.2	168.9	–	613.2	1174.6	418.4	1432.0
	Sancta Maria	4	3869.8	506.3	–	3142.0	4317.0	–	–
12	**Cieplice Zdrój**								
	Cieplice 2	25	134.5	8.2	–	117.9	145.0	109.8	159.3
	Cieplice 1	6	134.4	10.8	–	120.4	152.2	–	–
	No 4 (Nowe)	37	151.0	14.3	+0.25	123.5	183.2	108.0	193.9
	No 1 (Marysieńka)	36	158.8	20.4	+0.20	121.3	197.1	97.7	219.8
	No 6 (Basenowe-Męskie)	37	139.5	12.1	–0.03	107.3	167.8	103.2	175.8
	No 5 (Basenowe-Damskie)	38	141.6	10.7	+0.46	122.0	167.0	109.37	173.8
	No 3 (Antoni-Wacław)	37	179.3	25.8	+1.36	132.8	275.4	101.7	256.8
	No 2 (Sobieski)	32	301.6	69.6	–0.41	122.0	415.6	92.9	510.4
13	**Lądek Zdrój**								
	Dąbrówka	36	47.1	12.7	+0.77	11.7	80.8	9.0	85.3
	Jerzy	33	49.2	12.7	+0.93	33.1	76.3	11.2	87.2
	Skłodowska-Curie	34	46.0	13.3	+1.38	30.5	83.9	6.0	85.9
	Wojciech	36	47.8	13.3	+0.89	23.2	83.9	7.8	87.7
	Chrobry	36	45.4	13.3	+1.49	27.9	80.8	5.4	85.5
	L-2	20	41.4	10.0	–	24.4	66.5	11.3	71.6
	Stare	4	63.7	16.3	–	42.1	76.3	–	–
14	**Przerzeczyn Zdrój**								
	Siarczkowe	26	267.3	18.4	–	208.0	305.0	212.0	322.7
	No IX	15	270.1	9.3	–	254.0	290.7	242.3	298.0
	No II	8	296.8	28.4	–	269.7	335.6	211.6	381.9
	No XV	12	375.1	30.3	–	307.4	399.6	284.3	466.0
	No XIII	11	375.5	20.6	–	314.0	386.0	313.7	437.2
	No XI	11	374.6	16.3	–	346.8	394.0	325.6	423.7
	No VIII	14	355.4	23.9	–	278.0	381.4	283.8	427.1

ters and mineral waters not declared as therapeutic, which neighbour the therapeutic waters.

Normality of distribution is, however, concordant with an often observed phenomenon (Smirnow, 1963), that in groundwaters, the normal (symmetrical) distribution is one of the three most common ones. It occurs in conditions of chemical equilibrium or is a result of numerous, independent, anisotropically acting hydrochemical processes. The processes are added but none of them gains advantage over the other (Macioszczyk, 1977).

The TDS, however, is not an explicit feature for verification of the phenomenon described above. In the quantitative sense, mineralization of the Sudetic therapeutic waters and their hydrochemical type is decided most frequently by three, and in many cases even four ionic components, i.e.: HCO_3^- and/or SO_4^{2-}, Ca^{2+}, Mg^{2+} and Na^+. Therefore, normality of distribution may (according to Macioszczyk, 1977) result from overlapping of several independent processes averaging each other. Only the observation of individual components may bring a more precise solution to the problem of formation of the waters' chemical character.

The bicarbonate ion comes automatically, as it is present in waters of almost all intakes analysed as the principal anion (according to the Shtschukariev-Priklonski classification as quoted by Macioszczyk, 1987), being second only to the sulphate anion in some intakes. Its major influence on the total mineralization of the waters is also confirmed by strong correlation relations between the TDS and the $[HCO_3^-]$ content in the majority of therapeutic water intakes in the Sudetes (Ciężkowski, 1990; Ciężkowski *et al.*, 1996). It is also important that most of the waters analysed are carbonated waters strongly enriched in CO_2.

The predominant role of bicarbonates is typical of waters composition in the upper part of the earth's crust, in particular, in the moderate climatic zone, where the composition is formed due to weathering of primary silicates and aluminosilicates, and leaching of limestones and dolomites. Similar conclusions were drawn also in relation to hydrogeological structures of various types, from comparison of average chemical compositions of groundwaters from various parts of the world (Voigt, 1989).

The result of testing of the $[HCO_3^-]$ content in 68 Sudetic therapeutic waters intakes was similar to the TDS distribution. The Kolmogorov test at the significance level $\alpha=0.05$ proved that $[HCO_3^-]$ content distributions of almost all intakes may be regarded as normal. It means that accepting the hypothesis that the samples tested come from a general population with a normal distribution, one makes an error lower than 5%. The only intake for which there are reasons for rejection of the hypothesis on the normality of $[HCO_3^-]$ distribution at the assumed significance level, is the 'Górne 2' intake in Świeradów Zdrój. The $[HCO_3^-]$ content distributions in waters not declared as therapeutic are of Gauss type.

DETERMINATION OF NORMAL VALUES OF HCO_3^- CONCENTRATION AND HISTOGRAMS ANALYSIS

Determination of normal values interval was done using the three standard deviations method (3σ) (e.g. Gawicz *et al.*, 1981; Roszak, 1991). This principle states that the probability of occurrence of a value from the interval (-3σ, $+3\sigma$), whose centre is the expected value (identified in the case of the normal distribution with the arithmetic average), is close to one and amounts exactly 0.9973. A graphic method, suggested by Macioszczyk (1977) was not applied due to a too small size of the majority of the samples. Lower and upper ranges of the intervals determined are presented in Table 1. In general, it may be noticed that the majority of the analyses fall within the interval (-3σ, $+3\sigma$), and only in less than 20% of the intakes single values from outside of this interval were observed.

However, for large samples, i.e. with $n \geq 30$ (border value for χ^2 distribution) some analysis of $[HCO_3^-]$ concentration histograms was carried out. The histograms were plotted for standardized variables, expressing the number of units of standard deviation by which the given value deviates from the arithmetic average (1) (Fig. 2):

$$z = \frac{x_i - \bar{x}}{\sigma} \qquad (1)$$

where:

z: standardized variable,

x_i : observed value,

$\bar{x}$: arithmetic average of values observed in the sample,

σ : standard deviation in the sample.

All possible distributions encountered in groundwaters were observed (except for j-shaped), i.e.: symmetrical, asymmetrical with positive skewness and asymmetrical with negative skewness, rarely encountered in groundwaters (Smirnow, 1963; Macioszczyk, 1977). In the 28 intakes analysed, skewness (asymmetry) coefficients A_X were calculated in an unbiased way according to the formula (2) (Luszniewicz & Słaby, op. cit.) (Table 1):

$$A_x = \frac{n}{(n-1)(n-2)} \sum \left(\frac{(x_i - \bar{x})^3}{\sigma^3} \right) \qquad (2)$$

where:

n – sample size, other symbols as in (1).

The most common distributions are these with the positive skewness (20 intakes), usually with asymmetry coefficient above +0.5. 8 distributions skewed to the left were observed with asymmetry coefficient usually not lower than –1.0. As a rule, similarly as in the TDS distributions, the author did not observe a general dependence of histogram shapes (including their skewness) on the absolute mineralization value, intake depth, or proportion of common waters component.

In addition, a lot of the distributions reveal bimodality which eliminates the diagnostic value of the arithmetic average (Kassyk-Rokicka, 1986) and indicates a heterogeneity of the sample. Nevertheless, relatively small sample sizes and the lack of reasons for rejection of the hypotheses on normality of general populations distributions, allow the application of the statistical method for determination of normal values. However, in the bimodal samples case, these values, determined with the 3σ method should be treated

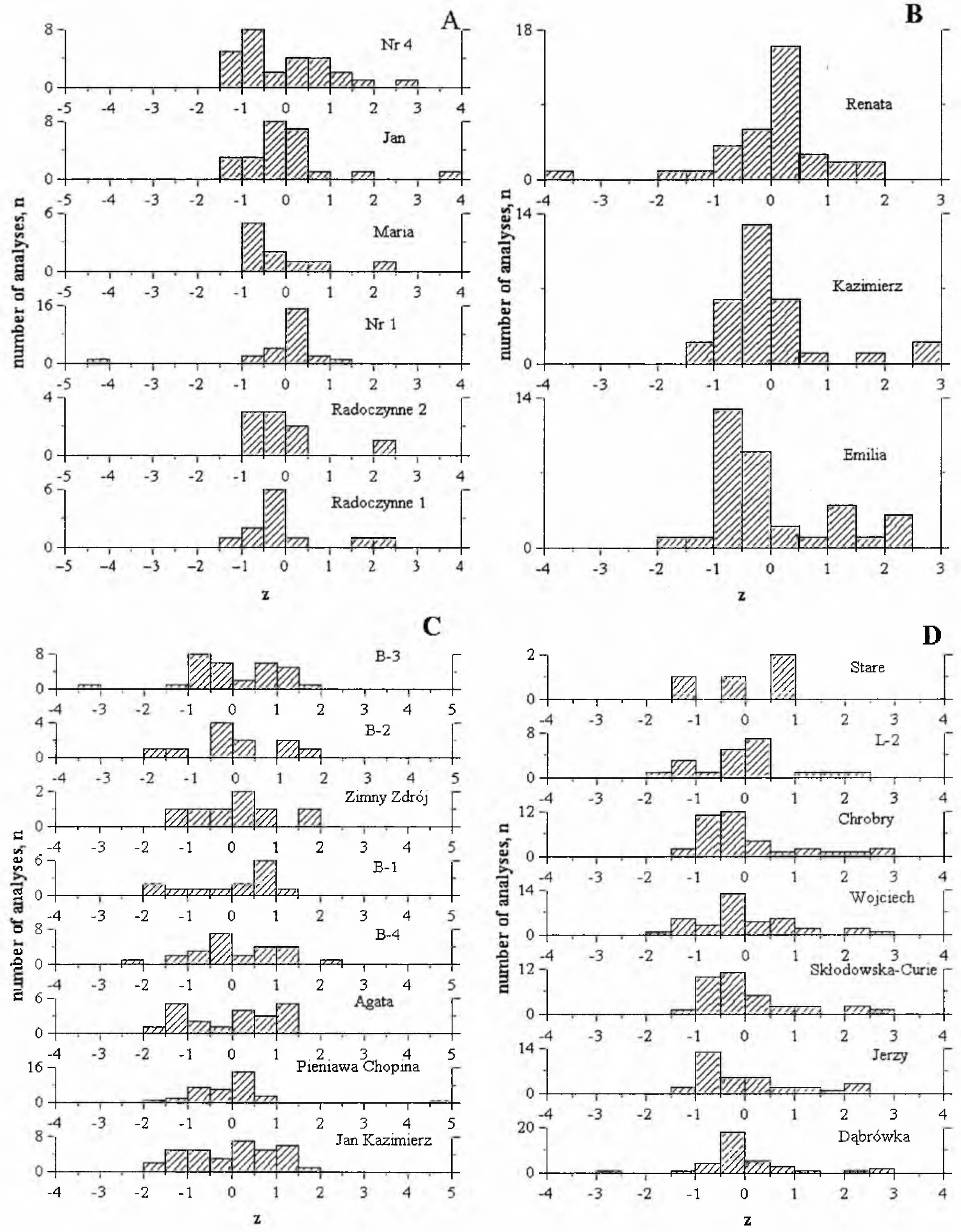

Fig. 2. Histograms of standardized $[HCO_3^-]$ concentrations in selected Sudetic therapeutic waters from: A – Czerniawa Zdrój, B – Długopole Zdrój, C – Duszniki Zdrój, D – Lądek Zdrój. z – standardized $[HCO_3^-]$ concentrations were calculated according to the formula (1) (see text)

with caution. In particular, the interval borders for two populations distinguished (corresponding with the two peaks) should be determined. The normal values would be represented by an interval representing the larger population; this was, however, abandoned because of the reasons presented before.

$[HCO_3^-]$ distributions in certain intakes display a significant concentration of analyses around the arithmetic average (e.g. 'Radoczynne 1' and 'Radoczynne 2' intakes in Czer-niawa Zdrój and 'Szczawina 1' in Szczawina) (Fig. 2). In such cases normal values intervals could be expressed more precisely, as e.g. the $(-1.5\sigma,+1.5\sigma)$ interval proposed by Weil (1981).

It is clear, that the accuracy of the normal HCO_3^- content intervals in individual intakes will be the higher the more new measurements will be taken under consideration.

DISCUSSION

It is assumed, that all Sudetic therapeutic waters are of infiltration origin or contain different fractions of fresh waters of shallow circulation (Ciężkowski, 1990; Ciężkowski *et al.*, 1996). Their final chemical composition results from mixing of two components, i.e. of the stronger mineralized component of the deeper origin, and the shallow, slightly mineralized one (Ciężkowski & Szarszewska, 1978; Ciężkowski, 1990; Ciężkowski *et al.*, 1996). When it comes to change of these proportion, comes also to change of the mineralization and chemical composition of mixture.

The observed normality of the considered chemical features' distribution in all Sudetic therapeutic waters bear evidence of their little variability during the whole exploitation period. The influence of analytical errors was reduced to the minimum using rigorous criteria of analyses selection (see: Method of investigation). The chemical analyses taken into consideration were carried out by the only two laboratories and in the same way in the whole time. Moreover, assuming after Weil (1981), that values outside the $(-5\sigma,+5\sigma)$ interval are false, such values are absent in the intakes under consideration.

It also should be noticed that the normality of TDS and $[HCO_3^-]$ distributions is only seemingly inconsistent with results of papers concerning directly or indirectly the Sudetic therapeutic waters chemistry (e.g. Ciężkowski, 1990; Ciężkowski *et al.*, 1996; Kozłowski, 1997). Results quoted in these papers confirm considerable fluctuations of the present infiltration waters proportion (background waters) (Ciężkowski, 1990) in the therapeutic waters exploited. It happens because the intervals of normal values $(-3\sigma, +3\sigma)$, expressed in absolute units (mg/dm^3), are often large and reach beyond real values (Table 1).

Long-term linear trends of mineralization decrease in therapeutic waters of three intakes in the Sudetes have been observed by Przylibski *et al.* (Górne 1, Górne 2 and Górne 3 intakes in Świeradów Zdrój – Przylibski *et al.*, 1998). As result of the little number of chemical analyses considered, it is hardly to state what process occurs there; whether steady, irreversible demineralization of therapeutic waters or long-term mineralization variability of sinuous type.

Then there are reasons to apply the 3σ-method for determining of normal values intervals. These intervals can be used for the results verification of monitoring the Sudetic therapeutic waters. The observed TDS or $[HCO_3^-]$ values reaching beyond the $(-3\sigma,+3\sigma)$ interval should be regarded as untrustworthy (false) and the measurement should be repeated. If the new measurement gives the same result there is a signal that in concerned therapeutic water underwent a sudden change of its TDS and $[HCO_3^-]$ content and probable also of other chemical components.

CONCLUSIONS

Assuming, that TDS and $[HCO_3^-]$ concentration variability existing in the therapeutic waters reflect natural processes taking place in the system, it can be concluded:

1) Sudetic therapeutic waters are characterized by a low variability of TDS and $[HCO_3^-]$ content in the whole exploitation period,

2) fluctuations of these features have a random character only; their most frequent values are comprised within a range of $+3\sigma \div -3\sigma$,

3) determined normal values intervals can be used for verification of monitoring measurements (the individually faulty measurements elimination) and/or may indicate sudden changes of chemical composition of the exploited therapeutic waters.

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Streszczenie

ANALIZA STATYSTYCZNA DWÓCH PODSTAWOWYCH WŁASNOŚCI CHEMICZNYCH (MINERALIZACJI I ZAWARTOŚCI JONU HCO$_3^-$) W WODACH LECZNICZYCH SUDETÓW

Jacek Kozłowski

W pracy przedstawiono wyniki analizy statystycznej dwóch podstawowych własności wód leczniczych Sudetów: mineralizacji (TDS) i zawartości jonu wodorowęglanowego (HCO$_3^-$) w 66 ujęciach z 13 miejscowości uzdrowiskowych Sudetów (Fig. 1) na podstawie rocznych analiz chemicznych tych wód. Parametry te, przetestowane dla 57 ujęć ($n \geq 8$) testem Kołmogorowa na poziomie istotności $\alpha = 0.05$, wykazują rozkłady normalne. Wykorzystując metodę trzech odchyleń standardowych (3σ) wyznaczono przedziały wartości najczęściej występujących dla zawartości [HCO$_3^-$] w poszczególnych ujęciach (Tabela 1). Tylko w około 20% ujęć stwierdzono pojedyncze wartości wykraczające poza ten przedział.

Dla zmiennych standaryzowanych *z* wykreślono histogramy rozkładu zawartości jonu [HCO$_3^-$] oraz przeprowadzono ich analizę (Fig. 2). Zaobserwowano cztery typy rozkładów zawartości HCO$_3^-$: symetryczne, asymetryczne ze skośnością dodatnią, asymetryczne ze skośnością ujemną oraz histogramy dwuwierzchołkowe (bimodalne). Dla 28 ujęć ($n \geq 30$) obliczono odciążone współczynniki skośności (asymetrii) A_X. Zdecydowanie dominują dodatnie współczynniki asymetrii (20 ujęć) – najczęściej powyżej +0.5; ujemnych zaobserwowano tylko 8 (zwykle o wartości nie niższej od –1.0).

Nie zaobserwowano zarówno dla rozkładów TDS jak i [HCO$_3^-$] ogólnej zależności kształtu histogramów oraz charakteru ich skośności od bezwzględnej wartości mineralizacji, głębokości ujęcia oraz udziału składowej wód zwykłych.

Normalność rozkładów TDS oraz zawartości jonu [HCO$_3^-$] w wodach wszystkich przeanalizowanych ujęć świadczy o dużej stałości tych parametrów przez cały okres eksploatacji. Obserwowane wahania powyższych parametrów mają wyłącznie charakter losowy. Pozwala to na wykorzystanie uzyskanych przedziałów wartości normalnych do weryfikacji wyników obserwacji stacjonarnych (eliminacji pojedynczych błędnych lub malo prawdopodobnych oznaczeń) i/lub sygnalizacji gwałtownych zmian składu chemicznego eksploatowanych wód leczniczych.